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FINAL TECHNICAL REPORT

Evaluation of Gallium Nitride for Active Microwave Devices

Office of Naval Research Contract N00014-81K-0567

Submitted by

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July, 1983

83 09 28 035

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. AD A132988	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* EVALUATION OF GALLIUM NITRIDE FOR ACTIVE MICROWAVE DEVICES		5. TYPE OF REPORT & PERIOD COVERED Final Technical Report 6/81 - 9/82
		6. PERFORMING ORG. REPORT NUMBER N/A
7. AUTHOR(s) M. Gershenzon		8. CONTRACT OR GRANT NUMBER(s) N00014-81-K-0567
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Southern California University Park Los Angeles, CA 90089-0241		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS PE 61153N RR021-02-03 NR 243-040
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research, Code 414 800 North Quincy Street Arlington, Virginia 22217		12. REPORT DATE July, 1983
		13. NUMBER OF PAGES 30
14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)		15. SECURITY CLASS. *(of this report)* UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

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18. SUPPLEMENTARY NOTES

ONR/Scientific Officer
Tel: (202) 696-4218 (YODER)

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Gallium Nitride
Molecular Beam Epitaxy
Photoluminescence

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Low temperature photoluminescence results reveal that donors in GaN are relatively shallow, so that low resistivity n-type material at room temperature is easily achieved. However, all "shallow" acceptors are quite deep, so that low resistivity p-type material is not possible. Thus, high current density, p-n junctions are not feasible. A native shallow donor, probably a simple nitrogen vacancy, is present in all GaN crystals grown, whether by VPE, MOCVD, and from these results, by MBE. It is present in the range $10^{18} - 10^{20} cm^{-3}$.

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20. Abstract (continued)

This doping level is much too high for it to be used in the drift region of an IMPATT device. Its value can be reduced by compensation with acceptors. But this also lowers the mobility, leading to an increase of the required electric field to attain saturated drift velocity, thus negating the advantage. The native donor density cannot be reduced by altering growth conditions in VPE, MOCVD or MBE growth. It can, however, be somewhat reduced by ion implantation of N^+ ions, followed by a specified anneal. This, however, leads to a meta-stable situation wherein device degradation seems highly likely. Thus, in spite of its theoretical potential, GaN may not be a good candidate as a material for transit-time-limited, power microwave amplifiers.

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I. INTRODUCTION

Several materials parameters of GaN, which are deduced from the known intrinsic properties of this semiconductor, imply that GaN may be an ideal material for transit-time-limited power microwave amplifiers (IMPATTs, etc.). The low electron effective mass and the high optical phonon energy imply a large electron saturated drift velocity, and the large bandgap implies a large pair-production threshold and therefore, high reverse breakdown potentials. Together, these parameters predict a materials figure of merit for GaN as a power amplifier that is 20 times better than that for Si.

Under a previous ONR contract, summarized in its Final Technical Report of September, 1980,[1] we had set out to grow semiconductor quality single crystals of GaN of high structural perfection and purity, to prepare both n and p-type material, to fabricate p-n junctions and Schottky barriers and to measure the saturated drift velocity and the pair production threshold as a prelude to constructing working devices.

As described in that final report, the first task, crystal growth, was difficult from the start. The estimated melting point of GaN is greater than $2,000^{\circ}C$, with a corresponding equilibrium pressure of N_2 of greater than 100,000 atm! For LPE growth conditions, based upon a liquid containing 10%N, the predicted melting point is $1500^{\circ}C$, with a N_2 overpressure of 18,000 atm, effectively ruling out that technique. The key, to the successful growth of GaN came from the observation that below $1100^{\circ}C$, the homogeneous dissociation of NH_3 into N_2 and H_2 is very slow kinetically. At 1050°, the equilibrium pressure of N_2 over GaN is 200 atm. At that same temperature, 200 atm of N_2 and 1 atm of H_2 should be in equilibrium with only 5 torr of NH_3, i.e. 5 torr of NH_3 is thermodynamically equivalent to 200 atm of N_2, the equilibrium pressure of GaN at 1050°. However, because of the sluggishness of the kinetics at this temperature, 5 torr of NH_3 can exist without the 200 atm of N_2 and thus prevent decomposition and allow crystal growth of GaN. Under

these conditions, the solubility of NH_3 in Ga is too low to permit LPE growth. Thus, vapor phase epitaxy (VPE) in which GaCl reacts with NH_3 in a standard hot-wall (halide-hydride) reactor at $1050°C$ was tried. After considerable effort, successful growth of epitaxial layers on sapphire was achieved. This included thick layers (5 mm), defect-free layers (only a few stacking faults and dislocations), and planar surfaces (on basal plane substrates). (More recently, we have achieved most of these same results using an MOCVD growth technique[2].)

However, all the crystals grown (including those grown by MOCVD) were heavily doped ($10^{18} - 10^{20} cm^{-3}$) n-type. At these very high concentrations, it was easy to rule out almost all chemical impurities as the cause, although, perhaps not H, O and C. Moreover, at these electron densities, the crystals were degenerate, with no carrier freeze-out occurring upon lowering of the temperature. Thus, the temperature dependence of the Hall effect provided no information about this shallow donor. Low temperature ($4.2°K$) photoluminescence, however, was found to be successful in characterizing the individual donors and acceptors, even in the presence of the degenerate electron concentration. In the Final Technical Report of the previous contract, we concluded that, based upon observations of bound exciton, donor-acceptor and free-to-bound transitions, (1) there are a number of shallow ($E_D \sim 30meV$) donors in GaN, (2) the shallowest acceptors are relatively deep (>200meV), thus, low resistivity p-type GaN at room temperature cannot be expected, and (3) the shallow donor responsible for the observed high electron concentration at room temperature, is probably a native defect.

This ubiquitous shallow donor prevented us from preparing material ($\sim 10^{17} cm^{-3}$) suitable for saturated drift velocity and pair-production energy measurements. (Although compensation with acceptors could be achieved, the resultant reduced mobilities negated the effects of compensation.)

II. GOALS

The aims of this contract were given in the Proposal and were succinctly summarized in the Work Statement:

1. Complete low temperature photoluminescence analysis of samples ion implanted with expected donors, acceptors and anticipated common impurities, determining energy levels and carrier type behavior for each.

2. Continue and complete photoluminescence characterization of samples ion implanted with Ga and with N as a function of implant dose and energy, and as a function of annealing time and temperature to determine if the native shallow donor can be reduced or otherwise influenced by the native vacancies or interstitials created by these treatments.

3. Grow GaN by MBE on GaN, sapphire and ZnO substrates, using as the N source first NH_3, then N_2 (with electron irradiation) and finally, a low energy ion source of N^+.

4. Measure carrier density and mobility on any high resistivity samples. If appropriate, proceed with saturated drift velocity and pair production measurements.

The accomplishments under this Contract will be described individually under these tasks.

III. ACCOMPLISHMENTS

1. The low-temperature photoluminescence program on doped GaN samples was completed. These results, integrated with the previous results, and including the methods of analysis of the experimental data, were presented at a recent opto-electronic conference.[3] A copy of that paper is appended to this report.

The chemical dopants investigated, including as-grown doping, intentional doping during growth, doping by diffusion, and, primarily, doping by ion implantation are summarized in Table I. The Ar implantation was used to establish the annealing procedure (three hours at 1000°C under NH_3 to prevent surface decompositon) to reconstitute the pre-implantation photoluminescence

spectrum, i.e., to completely remove implantation damage. A schematic diagram of the experimental arrangement for recording the low-temperature, near gap photoluminescence is shown in Fig. 1.

The results for shallow donors (effective mass-like, with small central cell corrections) is shown in Fig. 2. The deduced donor ionization energies are based upon the Haynes Rule, noting the linearity between measured bound exciton binding energy and donor ionization energy and calibrated by the observation of "two-electron" bands, corresponding to transitions which leave the neutral donor in an excited state. Note that the donor ionization range (15–50meV) is low enough to ensure that any of these donors (Se, Si, Ge, Sn or the native donor) will be more or less completely ionized at room temperature. Note also, that the "native" donor, always present, cannot be due to Se, Si, Ge or Sn.

TABLE I

DOPING

1. As-Grown – Native Donor, Si, C, O, Zn, Al

2. Doping During Growth – Si, C, O, Ge, Al

3. Diffusion – Li

4. Ion Implantation – Ar, Si, Ge, Sn, S, Se, Be, Mg, Zn, Cd, C, O,

   Li, Na, H, Ga, N

A similar plot for "shallow" acceptors is shown in Fig. 3. Here the Haynes Rule was calibrated from simultaneous donor-acceptor pair luminescence measurements at 4.2°K as confirmed by the observation of electron-to-acceptor, free-to-bound transitions at 77°K and described in the Appendix. The shallowest acceptor (Cd, 203meV), as a true effective mass acceptor corresponds to a hole mass ratio of 1.5. (A value of about unity was predicted.) Thus, these nearly effective mass-like acceptors (Cd, Ge, Be, Mg, Zn and Li) have ionization energies between 200 and 220 meV, a value much too large to provide significant ionization at room temperature. Hence, low resistivity p-type material at room temperature is not possible. Therefore, high current-density p-n junctions at room temperature are ruled out. This must include IMPATT devices as well as LED's and lasers. Schottky barrier structures, however, still remain viable.

Several other chemical species were considered as the possible origin of the "native" shallow donor, since chemical analyses could not rule them out, at least for C, O, and H. C, introduced by adding CH_4 during growth, by direct ion implantation and as a residual impurity, exhibits a photoluminescence band at 3.4615eV. This energy is too low for the Haynes Rule to be applicable. Hence it is a deep level (>250meV). Since the (n-type) resistivity increases with increased C incorporation, we conclude that C is a deep acceptor. Thus, it cannot be responsible for the "native" donor. O can be incorporated by adding H_2O during growth, by adding Ga_2O_3 to the Ga source during growth (yielding Ga_2O in the gas stream), by ion implantation and by its occurrence as a residual impurity. A photoluminescence band at 3.424eV is always associated with O. (A corresponding absorption band tails into the visible spectrum, rendering such crystals yellow in color if heavily doped with O.) This energy is also beyond the validity of the Haynes Rule. Furthermore, there is no significant change in resistivity of the n-type crystals when O is added. Thus, it is concluded that O is a deep donor. Al has been implanted and is often present as a residual impurity (probably from the Al_2O_3 liner

used in the VPE growth apparatus to shield the outer quartz liner from the halide species in the reactant stream to avoid reactions that liberate Si which will contaminate the growing crystals). As expected, Al is neither a donor nor an acceptor. It simply forms an alloy $Al_xGa_{1-x}N$ which increases the bandgap and shifts all photoluminescence peaks to higher energy. As much as 5% Al has been incorporated in as-grown GaN by using poor etching techniques to clean the Al_2O_3 liner. H is always present during growth, either from the H_2 gas flow dilutant or from the reaction of Ga with NH_3. Replacing the flow stream H_2 with N_2 does not alter the resultant photoluminescence. Proton implantation yields no new luminescence bands, nor does it enhance the native donor band. Thus, H cannot be associated with the "native" donor. In summary then, C, O, Al and H, which are always present to some degree, cannot be the source of the "native" donor.

2. We conclude that, since it cannot be associated with any chemical impurity, the "native" donor is indeed a native donor. Its ionization energy, from the photoluminescence results, is 26meV, and its concentration, from Hall data, is always in the 10^{18}-10^{20} cm^{-3} range. Its concentration is unaffected by growth parameters (NH_3 pressure or growth temperature). However, it is slightly perturbed by alteration of the substrate. In VPE growth on R-plane sapphire it occurs in the 2-7 x 10^{18} cm^{-3} range, whereas on basal plane sapphire, its density is higher, 5 x 10^{18} - 3 x 10^{19} cm^{-3}.[1] In MOCVD growth, it is more dominant, 1-6 x 10^{19} cm^{-3} on basal plane sapphire.[2] Thus, its incorporation must be controlled kinetically.

The most significant results of the recent experiments, show that the native donor can be influenced by implantation of Ga^+ and N^+ ions followed by the standard anneal under NH_3. Ga^+ implantation always increases the native donor luminescence; N^+ implantation always decreases it (see Fig. 4). (However, the changes are not large.) Hence the native donor must be due to an excess of Ga or a deficiency of N. The associated bound exciton peak,

appearing as a sharp line amid the normal shallow donor bound exciton lines indicates that the native donor is a point defect. To be associated with an excess of Ga or a deficiency of N, and to be a point defect, it therefore must be either a Ga interstitial, a N vacancy or an antisite Ga atom on a N site. The antisite defect should be an acceptor in violation of the observations. Thermodynamically, a Ga interstitial should be much harder to form in GaN than a N vacancy. Thus, we deduce that the native shallow donor is a simple N vacancy point defect.

The N^+ implantations, which reduce the native donor photoluminescence peak, should also reduce the electron concentration, increasing the resistivity. The thickness of the implanted layers, 2,000A, was too small, especially lying on the heavily n-type GaN substrate, to characterize by our standard electrical techniques, 4-point resistivity and Hall effect. However, such samples were characterized recently at Honeywell, Inc. by measuring the capacitance-voltage relation on Schottky barriers deposited on top of such implanted and annealed structures.[4] A dramatic increase of resistivity of up to three orders of magnitude, was observed, confirming the fact that the native donor can be reduced, and opening the possibility of obtaining low carrier concentration n-type material, without suffering the mobility loss when compensation by acceptors is used to reduce the electron concentration. However, some of this beneficial effect may be due to residual, unannealed, compensating acceptors. This would lower the net mobility, not a desirable feature.

3. At the time that this contract began, we had just acquired a Perkin-Elmer Model 400 (first generation) molecular beam epitaxy (MBE) system. Since MBE growth is usually almost completely kinetically controlled, without the imposition of thermodynamic constraints, it was anticipated that this method of crystal growth, with a wide range of controllable growth parameters, and the on-board analytical tools in the system, would offer the greatest

opportunities to control the native shallow donor as compared with other crystal growth techniques. In particular, the native donor incorporation mechanism should be associated with particular surface crystal structure patterns, observable with high energy electron diffraction (HEED), and these should depend on Ga/N flux ratios, as well as on substrate temperature.

During most of the scheduled period of this contract, the machine was being tested and calibrated (using GaAs growth as the base). Both technical and funding problems extended this break-in period. Thus, we asked for and received a no-cost extension to this contract. We have recently begun work on the MBE growth of AlGaN crystals under an Air Force contract.[5] Thus, the GaN MBE experiments, described here, served as a bridge between the calibration experiments and the current AlGaN work.

The basic growth mechanism in the MBE system was to be the reaction on the substrate surface of an atomic Ga beam (already existing and calibrated from the previous GaAs work) with a N-containing species. Basal plane sapphire, yielding good planar GaN growth in the VPE and MOCVD systems was to be used as the substrate, falling back on GaN itself, grown by MOCVD, if nucleation problems on sapphire became problematical. Again, we did not consider molecular N_2 as the N source, because, due to the strength of the N-N bond, dissociation on the growing surface would be slow, i.e. its sticking coefficient would be miniscule. Hence, we elected to use NH_3 again, with the knowledge that NH_3 reacts with Ga on the surface to form GaN by MOCVD at temperatures as low as $500^{\circ}C$.

A gaseous NH_3 effusion inlet was designed to produce an NH_3 beam whose angular divergence was comparable to the other molecular beams in the MBE system. This was built and installed in the center of the existing array of sources, and aimed at the center of the substrate. To avoid the possible condensation of NH_3, the inlet was not attached directly to the liquid N_2

cooled source housing. The inlet was fed by an ultrahigh vacuum leak valve from an ultrapure NH_3 gas cylinder and purge line. The NH_3 flux was calibrated vs. leak valve setting by using a calibrated bare Bayard-Alpert ion gauge in the sample position and using the theoretical ionization efficiency for NH_3. These results were confirmed by following the pressure in the growth chamber, with the pumps valved off, as the NH_3 pressure built up with time. In addition, the quadrupole mass spectrometer, adjacent to the substrate position, was used to confirm the total flux rate, as well as to establish the NH_3 cracking pattern when no crystal growth reactions occurred. As expected, the cryopump, the dominant pump in the MBE growth chamber, was very effective for pumping NH_3. But, because large amounts of NH_3 were used in each run, the pump became saturated rapidly and had to be regenerated after every two or three runs. After a run, the remaining NH_3 adsorbed on the walls could be removed easily. Normal pumping for two or three days, or an overnight bakeout, reduced the residual NH_3 pressure to less than 10^{-11} torr.

Some problems were encountered using basal plane sapphire as the substrate. First, the substrates would not stick and hold to the Mo substrate block using a thin film of In as the intermediate layer, a technique universally used for holding GaAs substrates. When the sapphire was polished on the back surface as well as on the front surface, the wetting and sticking problem was diminished considerably. Second, the sapphire substrate, after H_3PO_4 etching and washing with water, exhibited considerable outgassing when heated in the UHV environment of the MBE system. To avoid contaminating the growth chamber, most of this outgassing was performed in the entry chamber under poorer vacuum conditions (10^{-5} torr).

All the preliminary growth experiments were done with the substrates at $700^{\circ}C$. To avoid the formation of Ga droplets on the surface, the flux ratio of NH_3 to Ga had to be at least 5 to 1 and preferably 10:1. The maximum NH_3 flux was established by the constraint that the flux be a true molecular beam,

i.e. that the probability of collisions between NH_3 molecules in the beam be small. Under these constraints, the Ga flux deduced produced a GaN growth rate of about 2,000Å/hr.

Under these conditions, when no free Ga was left unreacted on the surface, the surface morphology was good (fairly planar) as evidenced by the appearance of a sharply streaked HEED pattern, corresponding to the symmetry and lattice constant of GaN. Subsequent Bragg x-ray diffraction indicated that the layers were epitaxial basal plane single crystals, although from the widths of the diffraction lines, it was concluded that the definition of orientation is only within $\sim 0.1^\circ$ of the ideal orientation, at least a factor of 10 worse than that for VPE crystals. However, these layers are only 0.2 to 0.5 μm thick, and the effect of the underlying sapphire substrate may not have disappeared as effectively as on the thicker (> 2μm) VPE layers. These thin layers probably should have been grown on GaN itself (grown by MOCVD or VPE) or on ZnO, a substrate with a much better lattice match to GaN, in order to avoid interface problems, especially significant for thin layers.

Several of the grown layers contained large amounts (up to 3%) of incorporated oxygen, as indicated both by (on board) Auger surface analysis and by electron probe microanalysis. The NH_3 source tank was rechecked by mass spectrometry for O_2 and H_2O. These results were negative. We concluded that unpurged H_2O adsorbed on the walls of the NH_3 manifold was the problem. These lines were purged further while being heated. This apparently eliminated the oxygen problem.

Finally, and most significantly, the electrical properties of the grown layers was most disappointing. The layers were far too thin for the application of reliable contacts for Hall measurements. Thus, we relied on 4-point resistivity measurements. These resistivities (on the good, Ga-free samples) were very low, implying electron densities of about $10^{19} cm^{-3}$. Thus,

it is concluded that MBE growth of GaN from Ga and NH_3 (without an extensive investigation of carrier density vs flux ratio and growth temperature) produces crystals with about the same shallow donor concentration as those grown by VPE or MOCVD. Moreover, in MBE growth, impurity contamination cannot be a problem (except for oxygen, which, however, is not a shallow donor). Hence, MBE growth, like VPE and MOCVD, yields crystals heavily doped ($\sim 10^{19} cm^{-3}$) with the native (N-vacancy) shallow donor.

In the proposal for this contract we also indicated two other approaches, other than NH_3, for obtaining the required N species. First, we proposed using a N_2 flux and using electron impingement on the substrate (from the HEED electron beam system) to try to dissociate the N_2. Simple calculations, however, showed that with the short dwell time of N_2 on the surface, such interactions would be negligible. Second, we proposed to use a high electric field ionizer to obtain a flux of charged particles (from NH_3 or N_2) in order to increase surface reactivity. In view of the required NH_3 to Ga flux ratio of close to 10 this ratio might be moved closer to unity. However, as stated in the proposal, this task was predicated upon the acquisition of an ionizer. The latter was part of a contract proposal (to ARO) which was not funded. Hence, ionized beams of N containing species were not tried.

Since the start of this contract, two Japanese groups have used MBE to grow GaN, one of them using partially ionized beams. Kimata and his students[6,7] at Waseda University, in a low quality vacuum (1 x 10^{-6} torr), home-built MBE system, have grown GaN on basal plane sapphire. Using an NH_3 source of N, single crystal epitaxial layers could be grown at a temperature as low as $625^{\circ}C$. By adding some N^+ ions to the beam from an ionizer of N_2, this temperature for single crystal growth could be reduced to as low as 490°. The crystals were n-type, 10^{19}-$10^{20} cm^{-3}$, without the addition of ions. With the addition of the ions, the electron concentration could be somewhat reduced, to as low as $10^{18} cm^{-3}$. Gonda and his group at the Electrotechnical Institute

have been using MBE to grow AlN for a number of years. Recently, they have grown AlGaN and GaN as well.[8-10] Growth of GaN at 700° on basal plane sapphire from Ga and NH_3 yields n-type material with an electron density of 5 x $10^{20} cm^{-3}$ but the electron density decreases as Al is added. These are very thin layers on sapphire, still dominated by the poorly matching interface. If the GaN is grown on AlN (pre-deposited on basal plane sapphire) the resultant electron density is $10^{19}-10^{20} cm^{-3}$, matching our VPE, MOCVD and MBE results. Thus, the native shallow donor has not been eliminated.

4. In the proposal, it was noted that saturated drift velocity and pair production threshold measurements would be attempted if low electron density ($\sim 10^{17} cm^{-3}$) GaN samples could be achieved without resorting to compensation (lowered mobility). Such samples could not be obtained. VPE, MOCVD, and now, MBE grown layers of GaN are all dominated by the presence of a native shallow donor (a N vacancy) in the range $10^{18}-10^{20} cm^{-3}$.

CONCLUSIONS

Although the intrinsic properties of GaN lead to the prediction that this semiconductor should have a materials figure-of-merit for a transit-time-limited power microwave amplifier that is 20 times higher than that for Si, the realization of such a device is not likely. First, all "shallow" acceptors in GaN are relatively deep (>200 meV), so that room temperature low resistivity p-type material, and therefore large current density p-n junctions, are unlikely. Second, all GaN crystals grown to date (by VPE, MOCVD and, now, MBE) contain large concentrations ($10^{18}-10^{20} cm^{-3}$) of a native shallow donor (probably a simple N vacancy). This is much too large to incorporate into the drift region of an IMPATT structure. Compensation with acceptors (Zn, Cd, Li, etc.) is feasible, but these reduce the low field mobility, so that much higher electrical fields are needed to reach saturated drift velocities, where GaN can have an advantage over Si. The native donor density can be somewhat reduced by implantation of N ions, followed by an

anneal to remove damage. But, in a high current density device, one must wonder if these donors will return, leading to degradation of the device.

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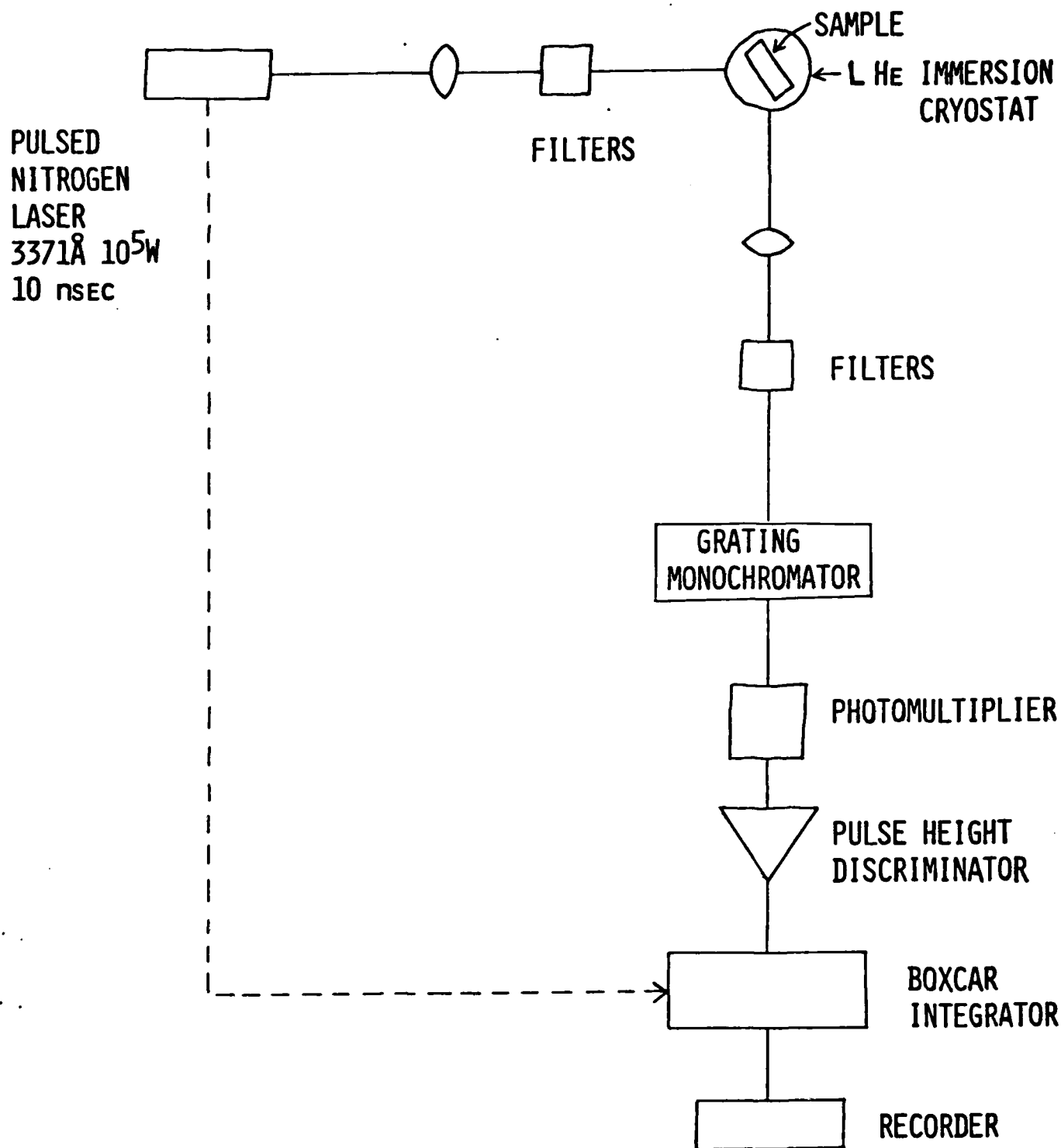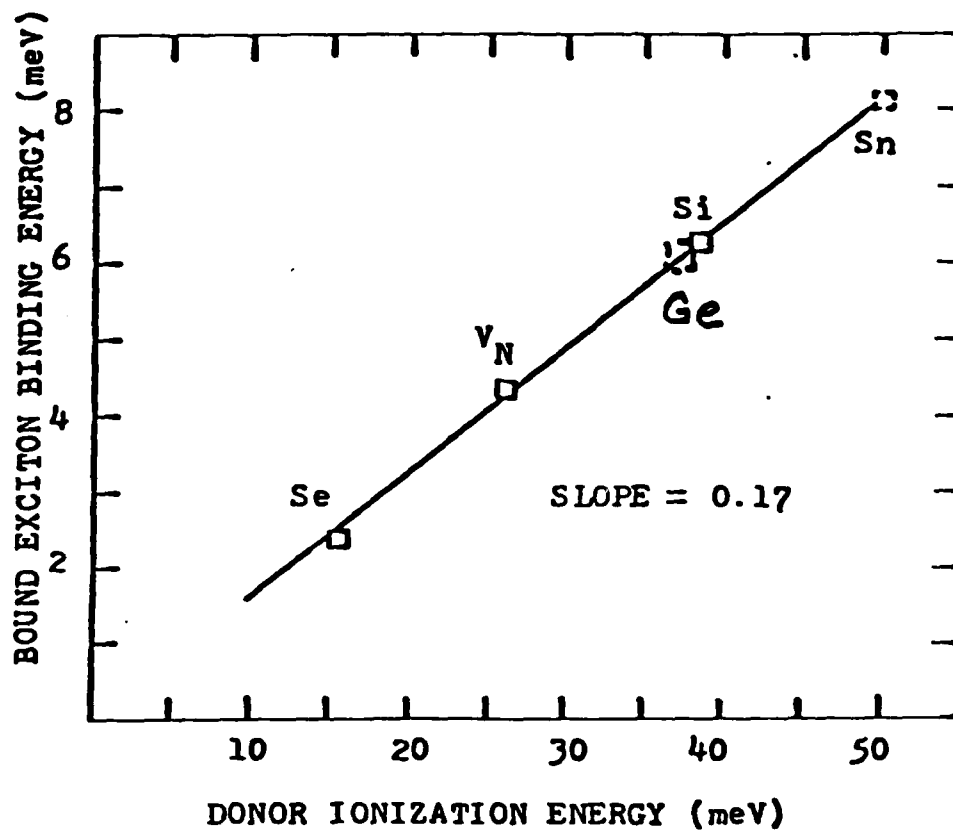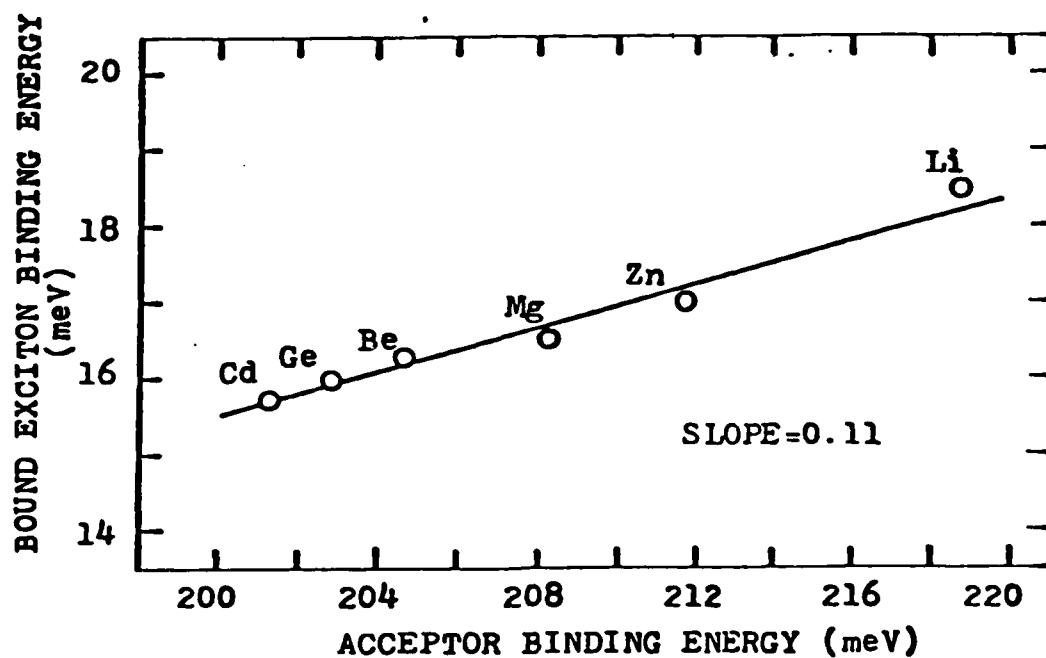
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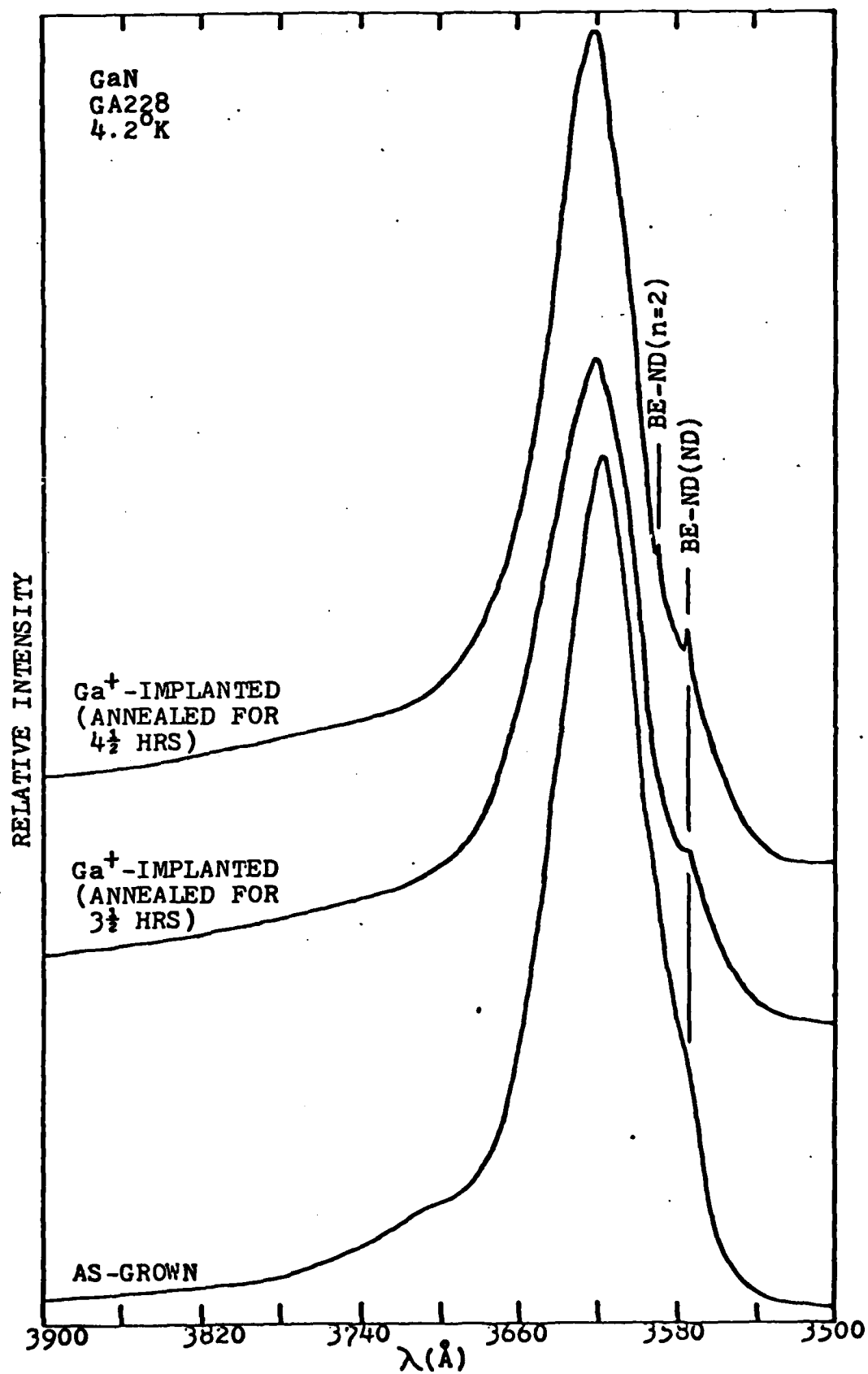
FIG. 1   PHOTOLUMINESCENCE SYSTEM

Bound exciton to neutral donor binding
energy as a function of donor ionization
energy determined from two-electron
transition and effective mass approximation

Fig. 2

Bound exciton to neutral acceptor binding
energy as a function of acceptor ioniza-
tion energy determined from D-A emission

Fig. 3

Photoluminescence spectra from typical Ga⁺ implant

Fig. 4

APPENDIX

GALLIUM NITRIDE: SHALLOW DONORS, DEEP ACCEPTORS, AND A SHALLOW NATIVE DONOR[a]

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ABSTRACT

The utilization of GaN as a material for UV LED'S, UV semiconductor lasers and transit-time limited microwave devices is limited by three major obstacles. First, crystal growth is accomplished only very far below the melting point by non-equilibrium growth techniques. Although structurally sound epitaxial single crystals can be grown by such techniques (halide-hydride VPE and OMCVD), native defect control has not been achieved. Second, all acceptors in GaN are relatively deep, so that low resistivity p-type material at room temperature cannot be obtained. Thus, high current, forward-biased p-n junctions are not possible. Third, a native shallow donor defect in the 10^{18}-10^{20} cm^{-3} range, probably a N vacancy, dominates all single crystals prepared to date. Control by equilibrium methods is not easily accomplished. Control by kinetic means has not been successful.

I. INTRODUCTION

GaN is a wurtzite structure, III-V semiconductor with a direct bandgap of 3.44eV (3600Å) at room temperature. As such, it becomes an ideal candidate as a material for UV semiconductor lasers and LED's. Furthermore, it offers the possibility of using a single materials technology for fabricating visible LED's over the entire visible spectrum. For this purpose, the visible light could be generated either via radiative deep-level recombination, or by coating a UV emitting diode with a down-converting, efficient, phosphor. To obtain the high radiative outputs needed for both a laser and an LED, a p-n junction device is needed.

A second potential device based on GaN is a transit-time limited (IMPATT) microwave power amplifier. Because the mass of nitrogen is small, the optical phonon energies are large. Combining this with the relatively small electron mass in GaN, $0.2m_o$, leads to a predicted saturated electron drift velocity much higher than that in either Si or GaAs. In addition, the large bandgap, resulting in a large pair-production threshold, would allow such a device to operate at relatively high voltages (below breakdown), a necessity for a power device. For such devices, a p-n junction is desirable, but a Schottky barrier structure will do.

We wish to show now, that there are three major problems associated with GaN that have made it impossible to achieve these goals at the present time, and that will probably be difficult to overcome in the future.

First, crystal growth is difficult. The attainment of high semiconductor quality crystals is not easy because the melting point of GaN is extremely high and the equilibrium N_2 pressure at the melting point is also extremely high. This leads to crystal growth by non-equilibrium methods, in which quality control is based not on thermodynamic considerations, but on the kinetics of the specific method chosen.

Second, because the hole masses in GaN are large, the shallowest effective mass aceptors are relatively deep, greater than 200meV. Thus, low resisitivity p-type material at room temperature is not feasible. Thus, lasers and LED's which are high current, forward biassed p-n junctions, cannot be made.

Third, the electrical characteristics of all GaN single crystals grown to date are dominated by the presence of a shallow, native donor, most likely a simple nitrogen vacancy. This is usually present in the $10^{18} - 10^{20}$cm^{-3} range. This donor can be compensated with acceptors to yield high resistivity material, but the donor itself has never been eliminated. Since the crystals are grown under non-thermodynamic

equilibrium conditions, reduction of this native defect requires consideration of the kinetics of growth, rather than a simpler thermodynamic understanding. Because of the presence of this native donor, material suitable for attaining saturated electron drift at high fields has never been achieved.

In this paper we first describe two non-equilibrium growth techniques that have yielded structurally sound single crystal epitaxial layers of GaN. These crystals are doped degenerately with the native shallow donor, so that electrical measurements are not useful for defining ionization energies of this donor, nor of other intentional and non-intentional dopants. Here, we turn to low temperature, near edge photoluminescence as the tool for characterizing the native donor as well as many other donors and acceptors introduced intentionally (mostly by ion implantation) or present is as-grown crystals.

II. CRYSTAL GROWTH

The true (maximum) three phase melting point of GaN should be higher than that of any other III-V compound because the energy of the covalent Ga-N bond is much larger than that between Ga and P, As or Sb. In addition, the equilibrium N_2 pressure should be high because the N-N bond in N_2 is much stronger than that in the other Group V elements.

From simplified thermochemical arguments, Van Vechten estimated the melting point of GaN to be 2970°C. By scaling the measured solubility of GaN in Ga ($\sim 10^{-3}$ at 1200°, Madar, et. al.) with the phase diagrams of GaP and GaAs, we estimate a melting point of 2400°. Thurmond calculated the heat of formation of GaN and used this to construct the 3-phase pressure-temperature relationship (well) below the true melting point on the Ga side of the phase diagram. This is a straight line on a log P vs $^1/T$ plot. By pressurizing a GaN crystal to a N_2 pressure P, then heating to a temperature T, then cooling and depressurizing, it is possible to tell which side of the phase boundary P and T were on, by noting whether the crystal melted. In this way, the phase boundary can be determined experimentally. We performed such experiments to N_2 pressures of 2,000 atm.; Madar, et.al. went to 4,000 atm; and most recently, Karpinski, et.al. have gone to 20,000 atm. The conclusion is that, to the highest T and P measured (1600°, 20,000 atm) the log P vs $^1/T$ curve is linear. As the true melting point is approached, however, this curve must bend over; T must go through a maximum ($^1/T$ through a minimum). By noting the bending observed in the Ga-P and Ga-As systems, we then estimate that the true melting point of GaN must be greater than 2400°C with a corresponding N_2 pressure of greater than 100,000 atm! Thus, growth of GaN at its melting point is next to impossible.

We next consider LPE growth from Ga and N_2, well on the Ga side of the Ga-N_2 phase diagram. At 1200°, where the N_2 equilibrium pressure is already very high (2,000-5,000 atm., Madar, et.al. and Karpinski, et.al.) the solubility of GaN is Ga is only 10^{-3} mole fraction. For a reasonable growth rate, and, to avoid constitutional supercooling effects, we require a solubility of at least 10^{-2} and preferably 10^{-1}. Thus, simple LPE growth must be ruled out.

The key to circumventing these thermodynamic obstacles is the use of a more reactive, but non-equilibrium form of N, namely NH_3. At 1050°C, the equilibrium pressure of N_2 over GaN and Ga (liquid) is approximately 200 atm. NH_3 will decompose into N_2 and H_2, and in order to obtain 200 atm. of N_2, we require sufficient NH_3 such that at 1050°, equilibrium is attained:

$$NH_3 \rightleftharpoons \frac{1}{2} N_2 + \frac{3}{2} H_2.$$
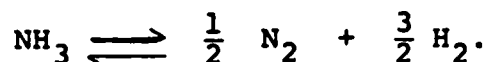
At equilibrium, if 200 atm of N_2 are required (obtained from NH_3, then 600 atm of H_2 will be formed) the final equilibrium pressure of NH_3 will be only 5 Torr!

The salient feature which allows the substitution of NH_3 for N_2 is that, below 1100°, the kinetics of the homogeneous decomposition of NH_3 into N_2 and H_2 are very slow. Thus NH_3 remains stable kinetically, and 5 Torr of NH_3 now become equivalent to 200 atm. of N_2 at 1050°.

We note parenthetically here, that GaN now becomes a catalyst for the dissociation of NH_3. At 1050°, GaN is slowly dissociating:

$$GaN \longrightarrow Ga + \frac{1}{2} N_2$$

But, at the same time, in the presence of at least 5 Torr of NH_3, the Ga released reforms GaN:

$$Ga + NH_3 \longrightarrow GaN + \frac{3}{2} H_2$$
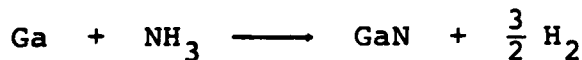
Thus, 5 Torr of NH_3 are necessary to keep GaN from decomposing at 1050° and the net effect of the GaN decomposition and reformation, is to convert NH_3 to N_2 and H_2, i.e. it is a catalyst for the reaction.

The possibility of using NH_3 in an LPE growth technique is ruled out because measured solubilities of NH_3 in Ga (the species present in the liquid has not been identified) is much less than 10^{-2} at 1050°C. Thus, we look for a vapor phase growth technique.

For a VPE growth technique, a GaN crystal is heated to 1050°, the highest temperature (rapid growth kinetics) at which an NH_3 pressure of 5 Torr will prevent decomposition. Ga must then be introduced as a vapor species. At 1050°, the vapor pressure of Ga itself is too low to allow reasonable growth rates. The only Ga species stable here at sufficient concentration are halides and metal-organics. Both VPE methods have been used to grow GaN.

In the hot-wall halide-hydride reactor, shown in Fig. 1, GaCl is formed by reacting HCl with liquid Ga in a H_2 ambient. Sufficient surface area of the Ga is provided to (almost)

completely convert the reacting HCl to GaCl, according to
the equilibrium constant for the reaction at 950°. The
GaCl is mixed with NH_3 and passed over the growing crystal.
In an attempt to decrease the nitrogen vacancy content
of the crystals, the effective NH_3 pressure was raised far
above the 5 Torr. required. Here the NH_3 would react with
the Ga in the source boats directly to form GaN on the sur-
face. Thus the NH_3 was introduced via a central inlet tube
so that it did not mix with the GaCl until just before the
substrate position. Growth rates of 10-60μm/hr were achieved
here.

For metal-organic growth, $(Me)_3$ Ga saturated H_2 was used
as the Ga source and reacted with NH_3 in a cold-wall reactor
(Fig. 2). Here the reaction with NH_3 is exothermic down to
room temperature. Thus the growth temperature is chosen as
low as feasible (850°) to allow good single crystal growth
rates (5μm/hr). Because of the formation of a low-tempera-
ture metal-organic-NH_3 addition compound, a solid, which
coated the cold walls and induced non-single crystal growth,
by dropping onto the heated substrate as particles, the metal-
organic species was introduced directly at the substrate
surface via an inlet tube close to one side of the substrate.
This resulted in non-uniform growth across the substrate.

The substrate chosen was sapphire. This more or less
matches the lattice constants of GaN. SiC or ZnO would have
been better matches, but these are not readily available as
substrate material and ZnO would have been chemically in-
compatible with the halide process.

On R-plane sapphire (cheap, used for silicon on sapphire),
thick single crystals-up to 5mm thick, but facetted, on
1x2 cm substrates - could be grown; but these were beset by
four problems. First, microcracks, originating from the sur-
face, would develop in layers greater than 200 μm thick.
Sapphire has a larger coefficient of thermal expansion than
does GaN. Hence, on cooling the crystal from the growth
temperature, the sapphire contracts most. It is in tension,
the GaN in compression. The resultant bimorph then bends,
concave on the sapphire side. If the GaN layer is thick
enough, although it is in compression close to the sapphire
interface, the bending moments put the free surface in
tension and if the thickness is greater than 200μm, it cracks.
For layers greater than 200 μm thick, this problem
can be eliminated by stopping growth below 200μm, re-
moving the substrate by grinding, and then continuing
growth. Second, microprecipitation (<100Å) of Ga occurs
at growth rates greater than 10μm/hr. These precipitates
decorated the growing interface periodically, but attempts
to make flow rates and substrate temperature more constant
did not improve the situation. Third, voids would form on
thick crystals due to the formation of re-entrant surfaces
(caves). These are equilibrium facets which form on the
growth surface of thick crystals. Reactant vapor species

and by-product vapors are kinetically restricted from entering and leaving these caves, and voids result. Slowing the growth rate below 10μm/hr relieves these kinetic considerations, and voids no longer occur. Fourth, the surface morphology is not planar. It is bounded by low energy prism-plane facets. Thus, good single crystal GaN can be grown on R-plane sapphire provided that the layers are less than 200μm thick (thicker if the sapphire is removed), and that the growth rate is less than 10μm/hr. However, the surface is non-planar.

GaN can also be grown on (more expensive) basal plane sapphire. Here the morphology is planar, and, at growth rates from 10 to 30μm/hr, only occasional stacking faults and dislocations mar the perfection of the crystals.

III. ELECTRICAL PROPERTIES AND DOPING

Crystals grown by the halide process were n-type with carrier densities between 10^{20} and 10^{21} cm^{-3}. Emission spectrography and spark-source mass spectrography showed that the dominant impurity was Si (a shallow donor, see below). Here, GaCl and unreacted HCl were reacting with the hot fused silica envelope of the growth apparatus to generate SiO which was incorporated in the growing GaN. A high density alumina liner was then installed in the growth apparatus, and the resultant crystals showed Si concentrations reduced below 10^{18} cm^{-3}. However, the electron density was still in the 10^{18} - 10^{20} cm^{-3} range. Chemical analyses showed no easily measured impurity in this range. Moreover, these samples were all degenerate, so that no freeze-out of carriers occurred upon reducing the temperature. Thus, Hall Effect and resistivity measurements vs. temperature provided no useful information. (Room temperature mobility vs. carrier density is shown in Fig. 3).

Hence, we turned to low temperature photoluminescence of samples as-grown and intentionally doped. Impurities in as-grown samples (as deduced below) included the native donor, Si, C, O, Zn and Al. Si, C, O, Ge and Al were intentionally added during growth. The melting point of GaN is very high, so that at 1050°, the highest temperature at which GaN is stable (under NH$_3$), diffusion coefficients are very small; only Li could be diffused in. The bulk of the doping experiments were accomplished by ion implantation. To accomplish this, we had to first learn how to remove the radiation damage caused by the implantation process. Here Ar implants were isochronally annealed at various temperatures in an NH$_3$ ambient. It was found that a 2 hour anneal at 1000° regained the photoluminescence spectrum observed for the sample before implantation. The dopants were implanted with energies to provide penetration depths of 2,000-3,000Å and with dosages to yield 5×10^{17} to 5×10^{19} cm^{-3} doped layers. The elements chosen included Si, Ge, Sn, S and Sn (expected donors), Be, Mg, Zn and Cd (expected acceptors), C, O, Li, Na and H (expected contaminants in as-grown crystals), and Ga and N (to alter the native defect density).

IV. LOW TEMPERATURE PHOTOLUMINESCENCE

High resolution, near-edge photoluminescence spectra were obtained from samples immersed in liquid helium and excited by a pulsed nitrogen laser, see Fig. 4. The laser wavelength, 3371Å (3.677eV) is slightly shorter than the bandgap of GaN at 4.2°K (3.504eV), and the absorption depth at this wavelength is about 2,000Å, equal to, or less than the ion implantation depth, so that unimplanted material is not excited. The laser emits 10^5 W of power in 10 nsec bursts. At such very high excitation densities, the carriers generated are expected to be quickly trapped by any ionized donors or acceptors present, so that all defects are quickly neutralized. Thus, luminescence should originate from neutral centers only.

If the exciting beam is sharply focused (1mm or less), a broad peak, well below the bandgap, appears in the luminescence spectra and dominates all other transitions. This has been shown to be due to the decay of an electron-hole liquid metallic phase. From such emission, the phase diagram of the eh liquid phase has been worked out previously vs. temperature, and, because GaN is a direct gap material, much of this luminescence is stimulated. In fact, laser action is observed if the emission is excited in a reasonable optical cavity with end reflectors. Hence, for the present work, the laser source was focused only slightly to avoid the appearance of this luminescence.

The only intrinsic emission expected is the free exciton. This has been observed previously in reflectivity and in luminescence at 3.475eV. It appears resolved in many of our spectra at 3.4744eV. The highest energy extrinsic emission should be due to the recombination of excitons bound to neutral, not ionized, shallow donors and acceptors. The Haynes' Rule, as observed in all normal semiconductors establishes a linear relationship between the binding energy of an exciton to a neutral donor (acceptor) and the donor (acceptor) ionization energy. The linearity constant, the Haynes' Rule constant, usually lies between 0.1 and 0.2. It is different for donors and for acceptors. This linear relation usually holds for donors and acceptors up to about 50meV deeper than the shallowest, effective mass, ionization energies.

An electron effective mass of 0.2 m_0 has been deduced for GaN. From this and the static dielectric constant, we conclude that the shallowest (effective mass) donor in GaN should have an ionization energy of 30meV. The Haynes' Rule then predicts that the binding energy of an exciton to such a neutral donor will be 0.1 to 0.2 of this value, or 3-6meV. For deeper donors, this value will be correspondingly greater. For acceptors, we guess that the hole mass is about $1m_0$, as in ZnS, with similar band structure and bandgap, predicting an effective mass acceptor ionization energy of 150 meV. Thus the binding energy of an exciton to such a neutral acceptor should be 15-30meV.

The photon energy emitted, corresponding to the decay of an exciton bound to such a center, should be the free exciton energy reduced by the binding energy of the exciton to the center. With a free exciton energy of 3.4744eV, we then expect the shallowest neutral donor bound exciton recombination to occur between 3.4714 and 3.4684eV (see Fig. 5). For deeper (non-effective-mass) donors, the ionization energy is larger, the binding energy for excitons is larger, and the emission will then occur at lower energies. For neutral acceptors, we expect the shallowest, effective-mass, levels to emit at 3.4594 to 3.4444eV, and deeper levels to emit at lower energies. Furthermore, as the levels become deeper, we expect the peak widths to increase, so that a donor transition lying below the shallowest acceptor might be distinguishable as a donor by its greater width.

In addition to bound exciton transitions, we also expect bound-to-bound transitions between an electron on a donor and a hole on an acceptor. This should yield a broad band whose peak position depends upon the donor-acceptor pair distribution, the recombination matrix element vs pair separation and on the excitation kinetics:

$$h\nu = Eg - (E_D + E_A) + e^2/\varepsilon r$$

For donors and acceptors in the $10^{18} - 10^{19} cm^{-3}$ range, the typical separation r at the peak of the emission is 100-200Å, with a corresponding Coulomb energy of 8-16meV. Thus, for donor-acceptor pair recombination between the shallowest donor

and the shallowest acceptor, we expect an emission band at 3.3404eV. This band should be broad owing to the participation of pairs of differing separation, and it should be replicated by the k=0 LO phonon of GaN. Pair recombination involving deeper donors or acceptors should occur at lower energies.

We now peruse a series of luminescence spectra of undoped (not intentionally doped) crystals grown by the halide-hydride technique. In Fig. 6, the free exciton peak (FE) is clearly seen. Two lines appear in the donor bound exciton range. (We will later show that ND, is the native shallow donor defect and that D_2 is a Si donor.) Two very weak lines, A_1 and A_2 fall in the shallow acceptor range. A deep level, or a series of deep level bands appear next at energies beyond the validity of the Haynes' Rule. Finally, a weak, broad Donor-acceptor band (DA) appears and is replicated by the LO phonon.

In the next spectrum (Fig. 7), the Si BE peak is reduced (alumina liner added to the halide-hydride VPE apparatus), a bound exciton acceptor peak is prominent (probably Zn, see below), little deep level bound exciton emission oocurs, but D-A bands are prominent.

In Fig. 8 a deep level bound exciton transition (I_d) becomes prominent, and in Fig. 9 such a deep level dominates the spectrum. (These bands will later be shown to be due to C and O.)

V. SHALLOW DONORS

Indentification of the shallow donors proceeds as follows. From the doping experiemnts, Si, Sn, Se and Ge produce sharp bound exciton transitions in the energy range corresponding to donors only. All samples exhibit the native donor bound exciton peak, also in this range. Thus we can determine the binding energy of an exciton to each of these neutral donors. The ionization energies of the donors themselves is determined in the following way. Most of these bound exciton transitions (Si, Se, native donor, particularly) are accompanied by a second (or even a third peak-Si) peak at lower energies. We assume that this is a two-electron transition that leaves the neutral donor in an excited state. We assume that this is the 2s state of the neutral donor (also 3s for Si). These are shown in Figs. 10 (Se) and 11(Si). We assume further that deviations from effective mass theory are much more marked for the 1s ground state than for the excited states with larger Bohr radii. Thus we assume that the difference in energy between the n=2 state and the ionization limit is given accurately by 1/4 of the effective mass Rydberg of energy, 1/4 x 30 meV here, and that the difference in energy between the observed 2 electron transition and the main bound exciton peak is the difference between the n=2 and the n=1 ground state of the donor, containing all the central cell corrections. Thus, the donor ionization energies are deduced. These data are given in Table I and are plotted in Fig. 12 as exciton binding energy vs. donor ionization energy. This yields a Haynes' Rule constant of 0.17 (within the 0.1-0.2 range predicted above) and from this, the ionization energies of Ge and Sn, for which no 2 electron peaks were observed, can be deduced merely from their bound exciton transition energies. These are included in Table I.

Se on a N site is expected to be a donor, as are Si, Ge, and Sn on a Ga site. The native donor, which dominates the electrical properties in undoped crystals, is here clearly identified as such. It is (so far) not associated with any intentional dopant.

It is noted that the shallowest donor ionization energy determined, that for Se, is just half of the effective mass donor energy originally predicted. This cannot be. If Se is assumed to be a true effective mass level, than the electron effective mass must be 0.1 not 0.2 m_0. The effective mass Rydberg must then be 15 not 30meV. Thus, the 1/4 of a Rydberg added to all the 2-electron to ground state shifts for the bound exciton must be reduced from 7.5meV to 3.75meV. Hence 3.75meV should be subtracted from all the deduced ionization energies. The Haynes' Rule relation remains linear, but the Haynes' Rule constant must be increased slightly, from 0.17 to 0.18.

VI. SHALLOW ACCEPTORS

Doping with Li, Be, Mg, Zn, Cd and Ge produces peaks just below the predicted limit for bound exciton decay at an effective mass neutral acceptor. Here no 2 electron transitions are observed to help determine the ionization energies. However, in all cases, DA pair bands appear strongly. The dominant donor, as observed from the shallow donor bound exciton emission, is the native donor, except for Ge, where it is the Ge donor. Since this native donor ($\sim 10^{19}$ cm^{-3}) is present at a higher concentration than any of the acceptors introduced, it alone determines the average pair separation. By comparing this with observations from other separations, we predict that the Coulombic energy at the peak of the emission will lie between 8 and 16meV. This energy is small compared with the acceptor energies about to be deduced.

In fact, the Coulombic energy can be deduced directly by the observation of free-to-bound transitions involving the same acceptor, but at higher temperatures (77°K), where the donors are rapidly ionized. These free-to-bound bands are distinguishable from the donor-acceptor bands, since the former are linear in excitation intensity, whereas the latter are sub-linear, owing to the complicated excitation and decay kinetics. A Coulombic energy of 14meV, corresponding to a pair separation of 113Å is deduced for the Cd doped samples.

Thus, the acceptor ionization energies are determined. These data are given in Table II, and in Fig. 13, the binding energy of an exciton to each of the neutral acceptors is plotted against the corresponding acceptor ionization energy, as derived from the donor-acceptor spectra. Here, a Haynes' Rule constant of 0.11 is deduced, again within the predicted range.

Note that all these acceptor ionization energies range from 201 to 219meV. All these "shallow" acceptors are rather deep, so that no low resistivity p-type GaN could exist at room temperature -- one of the unfortunate characteristics of GaN. If the shallowest acceptor observed here, Cd, is assumed to produce an ideal effective-mass level, than the effective mass of holes in GaN must be $1.3m_o$, a bit higher than first predicted.

Note that Be, Mg, Zn and Cd are expected to be simple acceptors on Ga sites, that Ge, in addition to behaving as a donor on a Ga site as noted above, should be an acceptor if on a N site. Li, however, might be expected to predominate interstitially as a donor. This is not observed. On a Ga site it should be a doubly-ionizable acceptor, hence, relatively deep. It is observed as a relatively shallow acceptor, although it is the deepest of all the shallow acceptors determined.

VII. DEEP LEVELS

GaN crystals were doped with a number of elements, all expected to be common impurities in normal crystal growth, primarily to see if any of them could be associated with the "native" shallow donor defect.

C was introduced by adding CH_4 to the growth stream and by ion implantation. It produces a broad luminescent band at 3.4165eV (with an LO replica). This energy is outside of the range of validity of Haynes' Rule for either the donors or the acceptors. Thus the luminescence cannot be used to distinguish which it is. However, the doped samples, although still n-type, always had a higher resistivity than the undoped samples. Thus C must be an acceptor, with an ionization energy greater than about 0.25eV. Many as-grown crystals exhibit this peak. Hence, C must be a common impurity, presumably on a N site.

O was intentionally introduced by ion implantation, by adding H_2O to the growth stream or by adding Ga_2O_3 to the Ga boats during growth. It produces a luminescent band at 3.4240eV. At very high concentrations it produces a strong absorption band which tails off into the visible, making the crystals appear yellow in color. No change in (n-type) resistivity was noted. Hence it is probably a deep donor on a N site. Not surprisingly, it is a common contaminant.

Na produces a band at 3.4527eV. This may be, like Li, an acceptor on a Ga site, but much deeper.

S produces a broad emission band at 3.4127. It must be a simple donor on a N site, but it is very deep.

Al was introduced intentionally by implantation, by adding Al to the Ga boat during growth, and, unintentionally, as an impurity. AlN and GaN are mutually soluble, and, as expected, Al simply increases the bandgap, shifting all peaks to higher energies. The shifts (at least up to 10% Al) seem to follow Vegard's Law.

H is obviously a common contaminant in all GaN crystals, whether grown by the halide-hydride or the MOCVD techniques. All reactant gases are diluted with H_2. NH_3 is the source of N. $(CH_3)_3Ga$ is the metal-organic source of Ga. Replacing the H_2 with N_2 in the halide-hydride VPE process produced no change in the photoluminescence of the crystals so grown. In particular, the "native" donor bound exciton luminescence was not affected. Proton implanted samples, after annealing, exhibited photoluminescence spectra identical to those before implantation, except for a slight reduction in over-all efficiency. Again, the native donor peak was neither enhanced, nor diminished. Thus, the ever-present H was eliminated as a possible source of this level.

VIII. THE NATIVE SHALLOW DONOR

The native shallow donor, with an ionization energy of 26meV and always present in the $10^{18} - 10^{19}$ cm^{-3} range, was not correlated with any chemical impurity, either by direct chemical analysis, or by noting the photoluminescence spectrum of crystals doped with a significant portion of the Periodic Table. Therefore, this donor is indeed a native defect. Its concentration is not easily altered by conditions of growth (growth temperature, NH_3 pressure), although its density does depend somewhat on sapphire substrate orientation (2-7 x 10^{18} cm^{-3} on R-plane sapphire and 5 x 10^{18}-3 x 10^{19} cm^{-3} on basal plane sapphire in halide-hydride VPE, and 1-6 x 10^{19} cm^{-3} on basal plane sapphire in MOCVD growth). MBE grown GaN (from NH_3 and N$^+$ sources) at temperatures as low as 490° (Kimata and Gotoh) are also n-type with carrier densities of about 10^{19} cm^{-3}. Thus, there is only a very slight kinetic control of this defect.

We have ion implanted both Ga and N at various energies and dosages, and gone through the annealing cycle described above, or have put the implanted samples through various isochronal annealing cycles, using photoluminescence as the characterization technique. Although quantitative results have not been meaningful, the qualitative conclusion is clear: Ga implants always intensify the native donor photoluminescent peak; N implants decrease it. Thus, the native donor, which we have already shown to be native, must be associated with an excess of Ga or a deficiency of N. From the sharp phtoluminescence peak close to the free exciton energy, we conclude that the defect must be a point defect. Thus it must be interstitial Ga, a N vacancy, or Ga on a N site (an anti-site defect). The last would be an acceptor and must be thus eliminated. Of the first two, the energy of formation of an interstitial Ga should be much higher than that of a N vacancy (Van Vechten). Hence, we conclude that the defect is a simple N vacancy.

A N vacancy should be a donor, in fact, a triply ionizable donor - an extension of the F-center from the alkali halides. That the first ionization is shallow may seem surprising. However, (1) the S vacancy in CdS is also very shallow, (2) much of the "central cell correction" to effective mass theory is due to the fact that the normal donor central cell atom is a foreign atom, not that of the host crystal (Pantelides); here, there is no such atom, it is vacant, and (3) lattice distortion effects should be small, since the (effective mass) Bohr radius of the bound electron is large, 45Å. Thus, the N vacancy could have such a shallow level.

IX. CONCLUSIONS

GaN, although an almost ideal candidate for a UV LED, a UV semiconductor laser and a high power microwave transit-time limited amplifier is beset by three major limitations.

First, crystal growth occurs under non-equilibrium conditions, so that crystal perfection can be obtained only with difficulty, and, control of the native defect density depends solely on the kinetics of the growth method.

Second, all acceptors are relatively deep. Low resistivity p-type material does not exist at room temperature, so that high current, forward biased p-n junctions are not feasible.

Third, the electrical properties of GaN are dominated by the ever-presence of a native shallow donor, a N vacancy, at concentrations of about 10^{19} cm^{-3}. While this native donor can be compensated, it cannot be reduced by current, non-equilibrium growth and annealing techniques.

Thus, GaN should be considered to be a pseudo-II-VI compound like ZnS, to which it is almost identical, or as a transparent metal.

Table I

Shallow donors in GaN

DONOR	BE-ND (eV)	TWO-ELECTRON TRANSITION (eV)	BOUND EXCITON BINDING ENERGY (meV)	IONIZATION ENERGY (meV)
V_N	3.4701	3.4517	4.3	25.9
Si	3.4681	3.4373	6.3	38.3
Sn	3.4662		8.2	50.0
Se	3.4720	3.4642	2.4	15.3
(Ge)	3.468		6.3	38

Free exciton energy is at 3.4744eV at 4.2^{O}K

Table II

		"Shallow" acceptors in GaN		
ACCEPTOR	BE-NA (eV)	BOUND EXCITON BINDING ENERGY (meV)	DONOR-ACCEPTOR PEAK ENERGY (eV)	IONIZATION ENERGY (meV)
Li	3.4559	18.5	3.2722	218.7
Be	3.4581	16.3	3.2861	204.8
Mg	3.4579	16.5	3.2826	208.3
Zn	3.4575	17.0	3.2791	211.8
Cd	3.4587	15.7	3.2896	201.4
Ge	3.4584	16.0	3.2756	202.9

The donor in the D-A transition is assumed to come from the native defect (nitrogen vacancy), accept for the Ge case, where it is assumed to be due to Si (or to Ge).
Free exciton energy is at 3.4744 eV at 4.2^{o}K
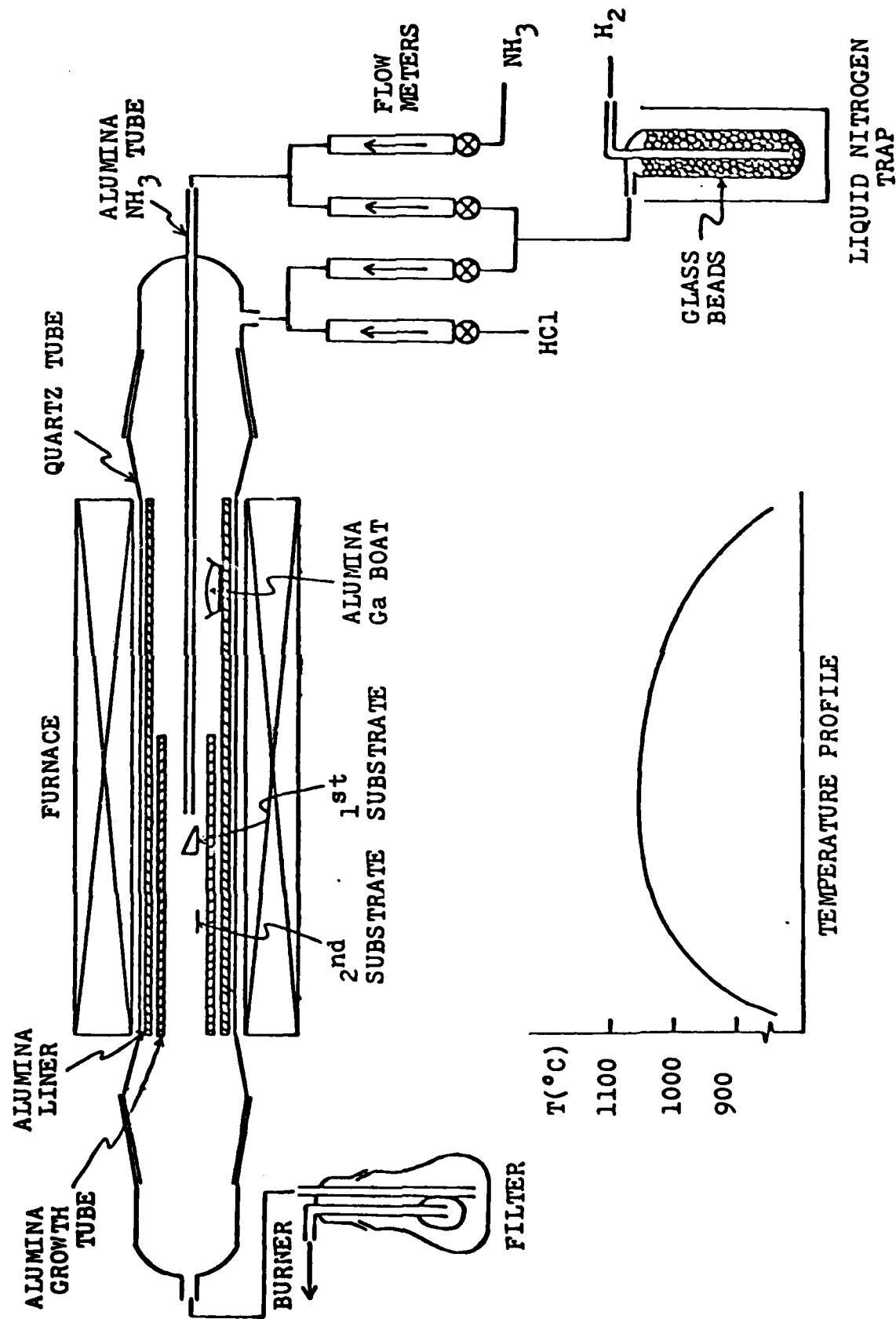
Halide-hydride VPE Growth System

Fig. 1
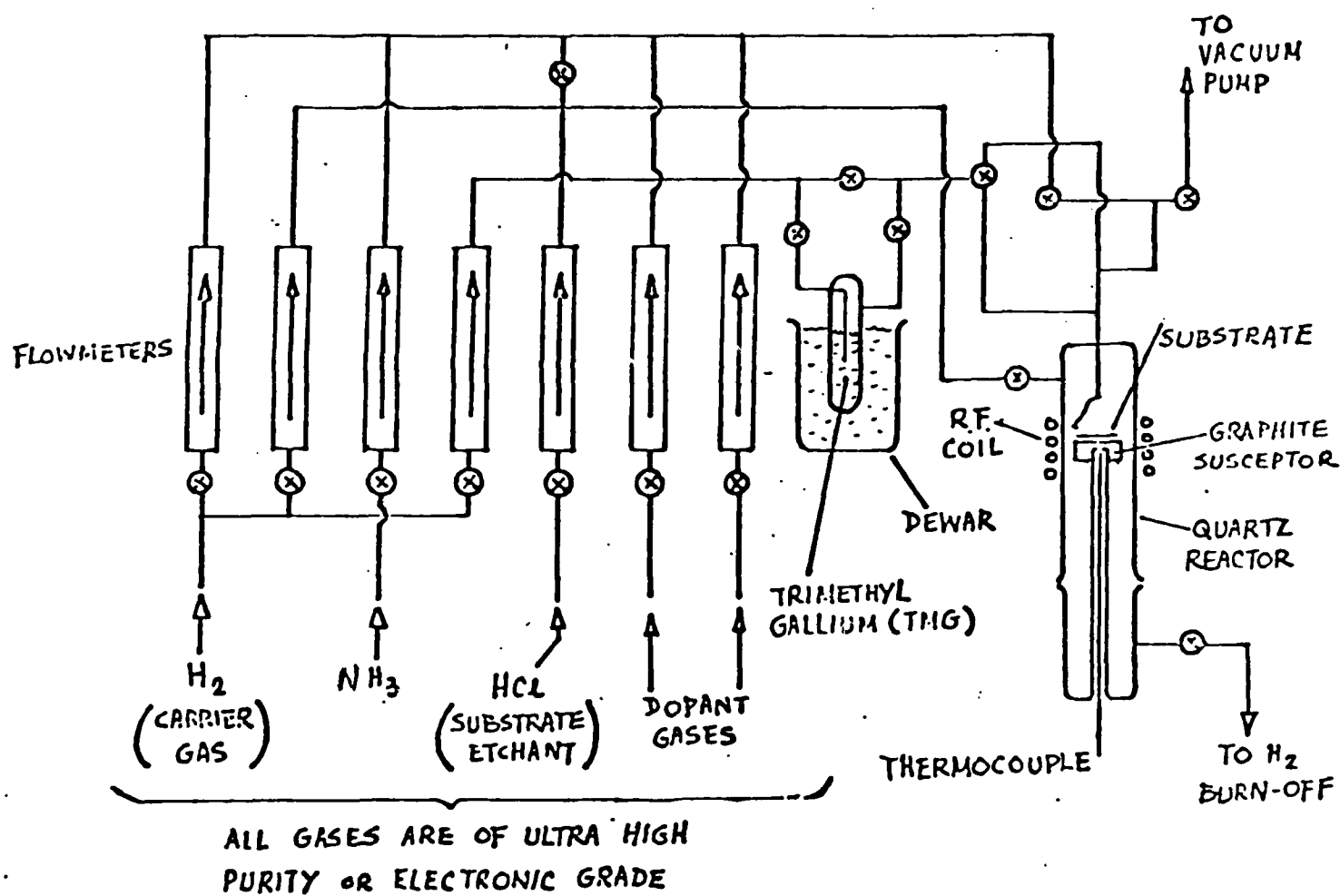
OM-CVD Growth System

Fig. 2
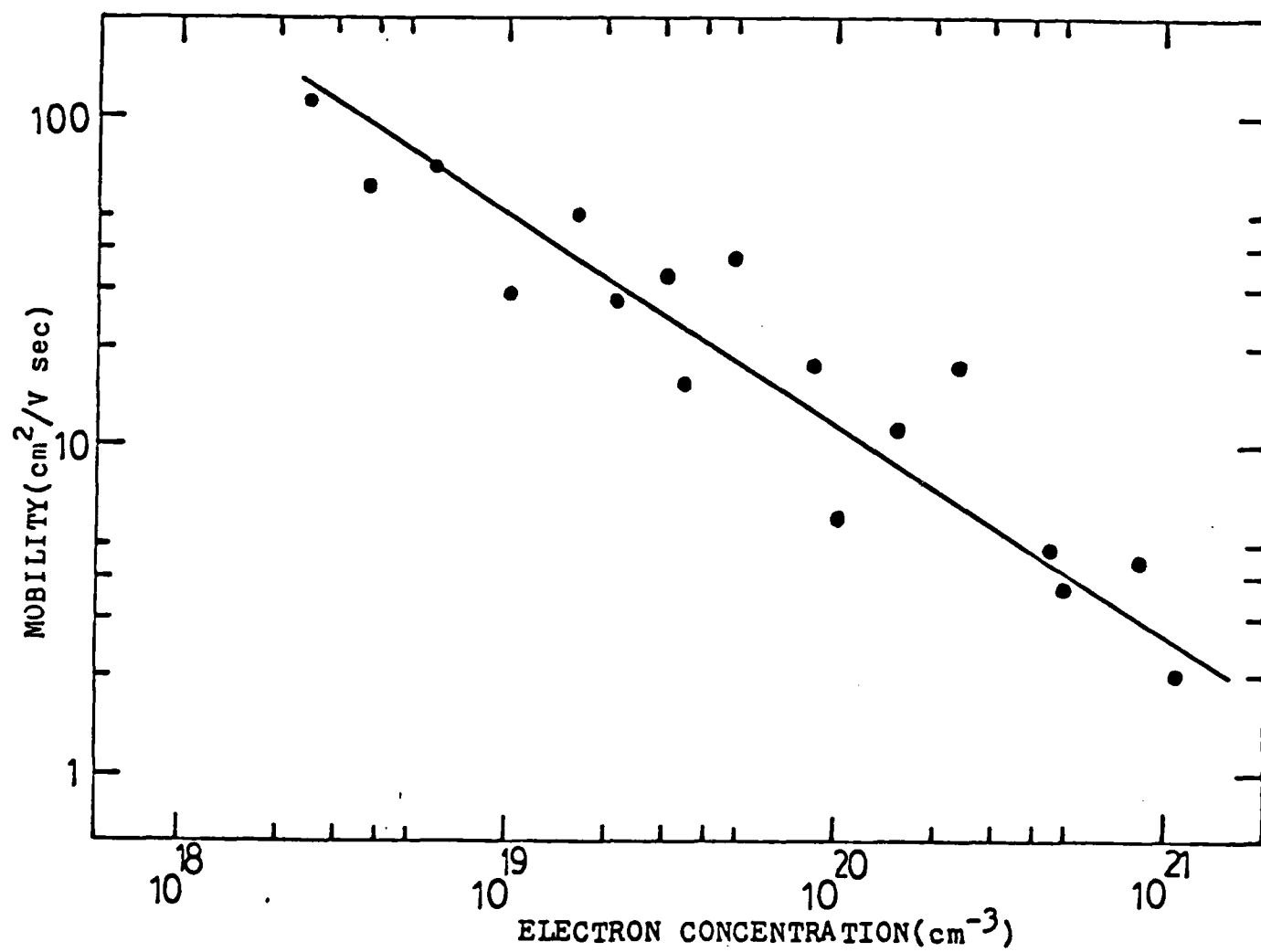
Room Temperature mobilities of as-grown GaN

Fig. 3
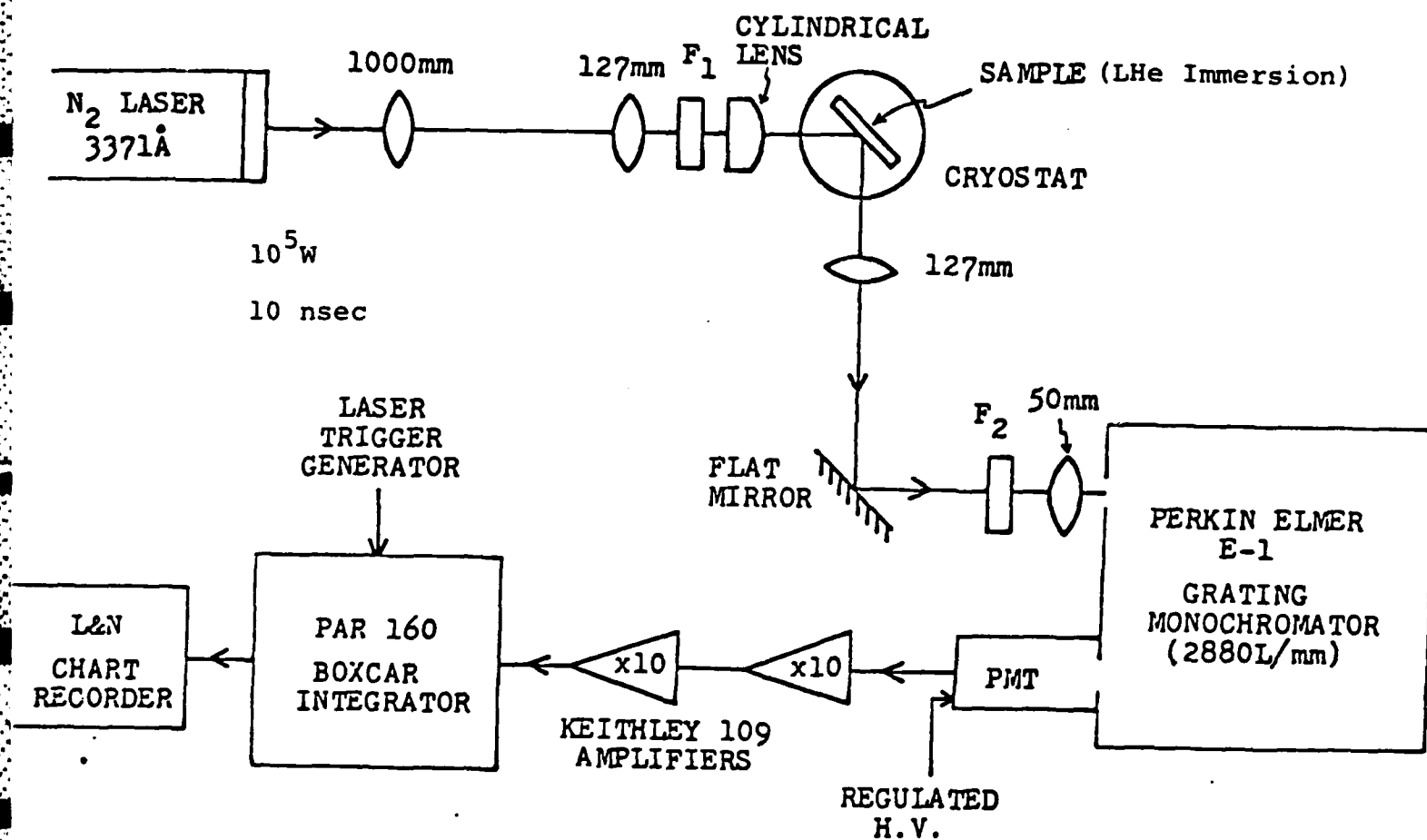
Photoluminescence Apparatus

Fig. 4

PHOTON
ENERGY
eV

```
(3.504)     3.505  ──┼──── Eg


(3.4744)    3.475  ──┼──── FE


(3.4714)    3.472  ──┼───┐
                         │  } BEND
(3.4684)    3.469  ──┼─┐ ┘
                       │↓
                       ↓


(3.4594)    3.460  ──┼───┐
                         │  } BENA
(3.4444)    3.445  ──┼─┐ ┘
                       │↓
                       ↓



(3.3404)    3.341  ──┼──── DA
                     │↓
                     ↓
```
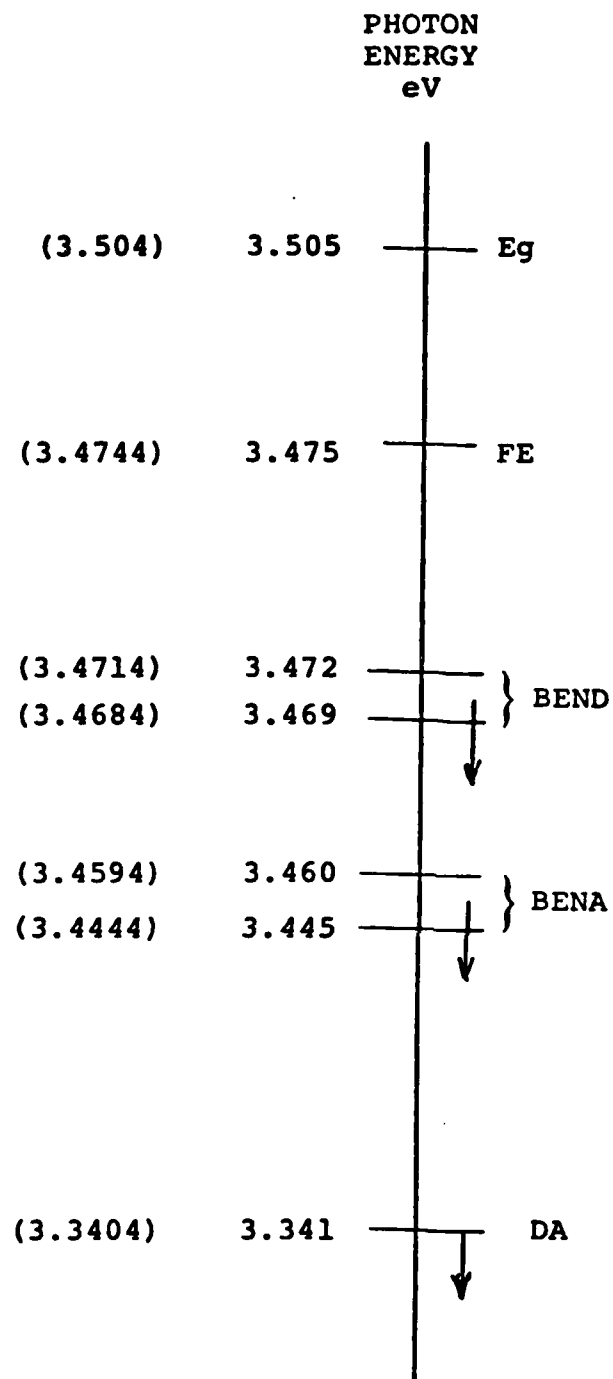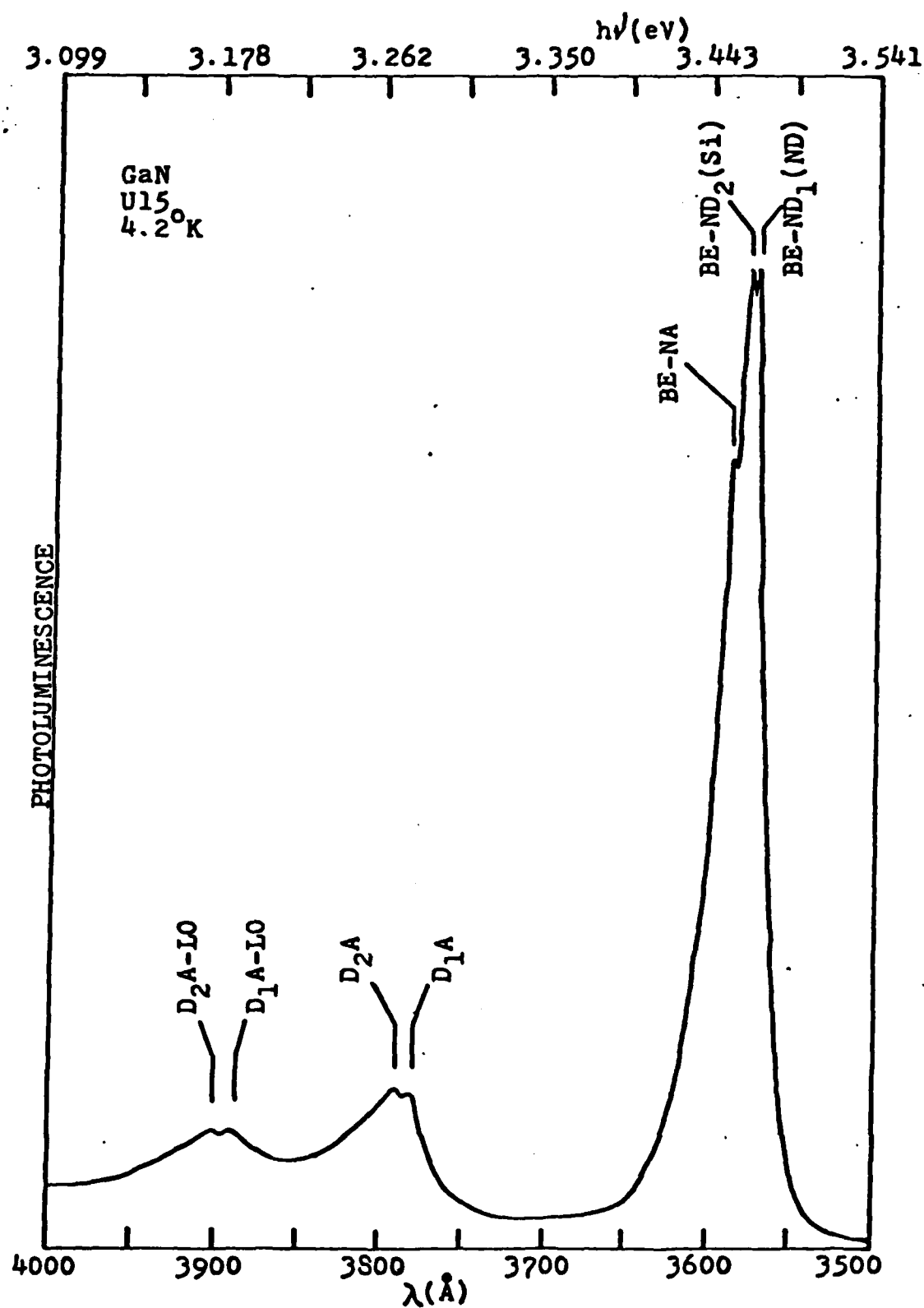
Predicted Limits of Expected Radiative Transitions

Fig. 5
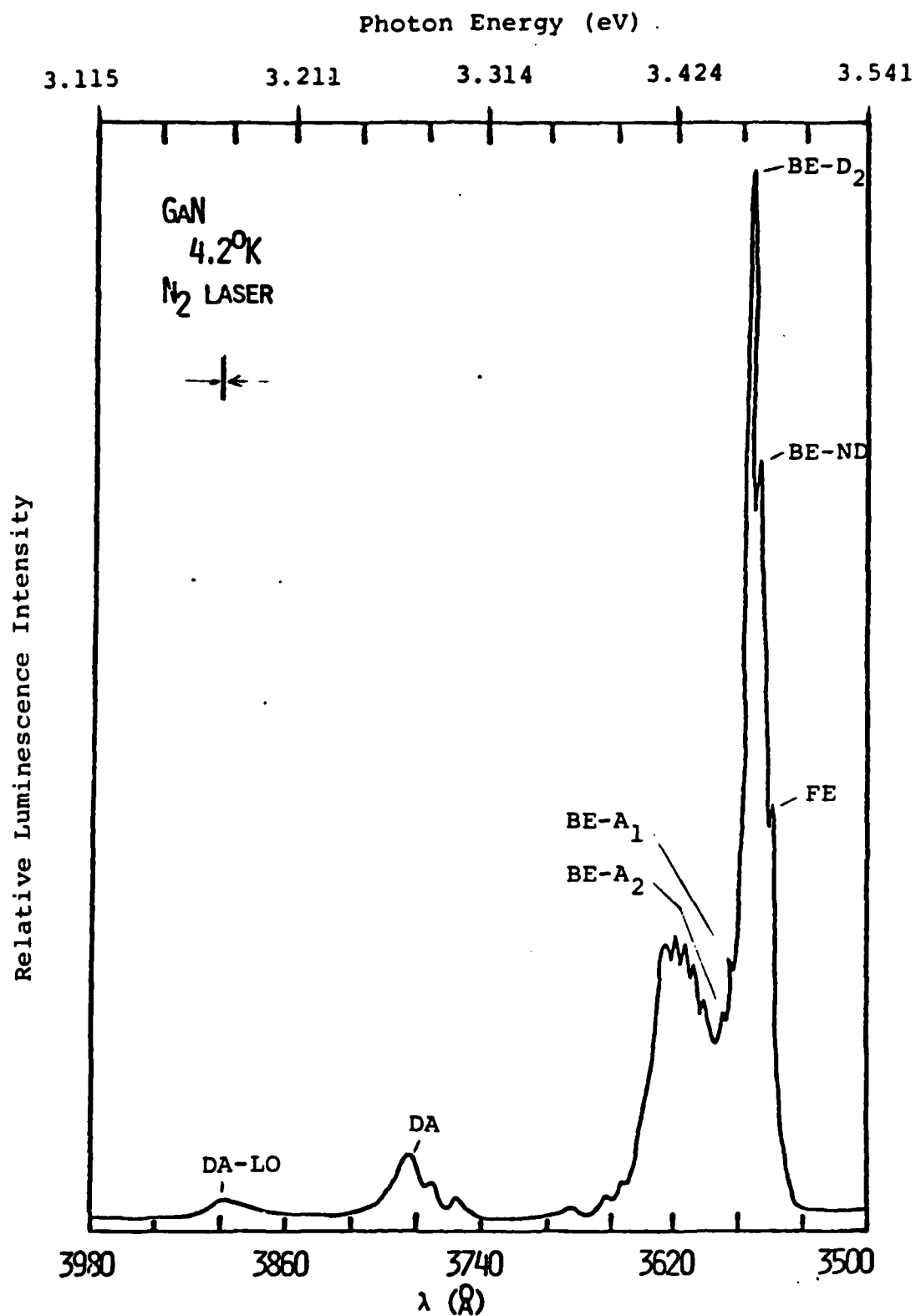
Luminescence of as-grown GaN

Fig. 6

Luminescence of as-grown GaN

Fig. 7
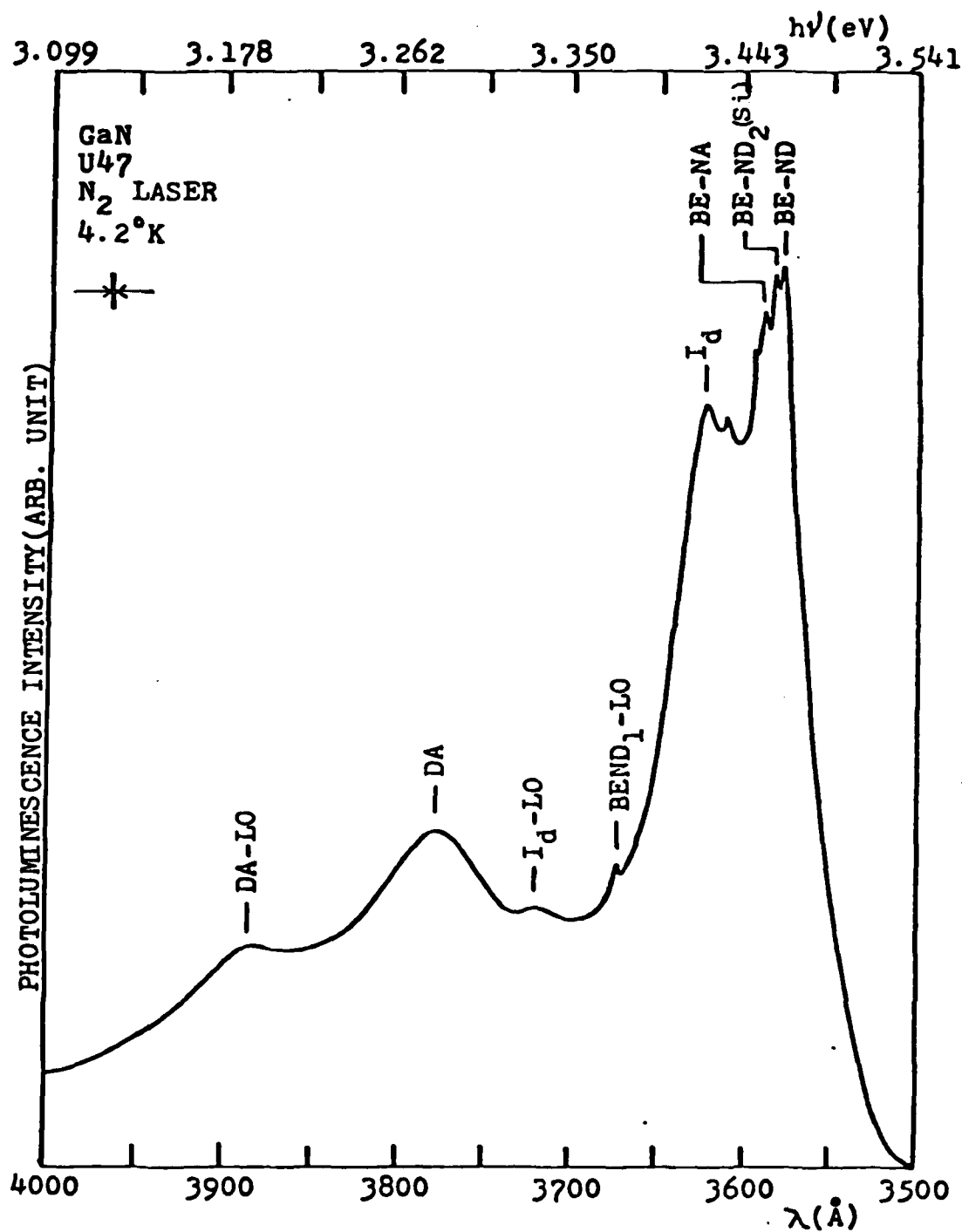
Luminescence of as-grown GaN

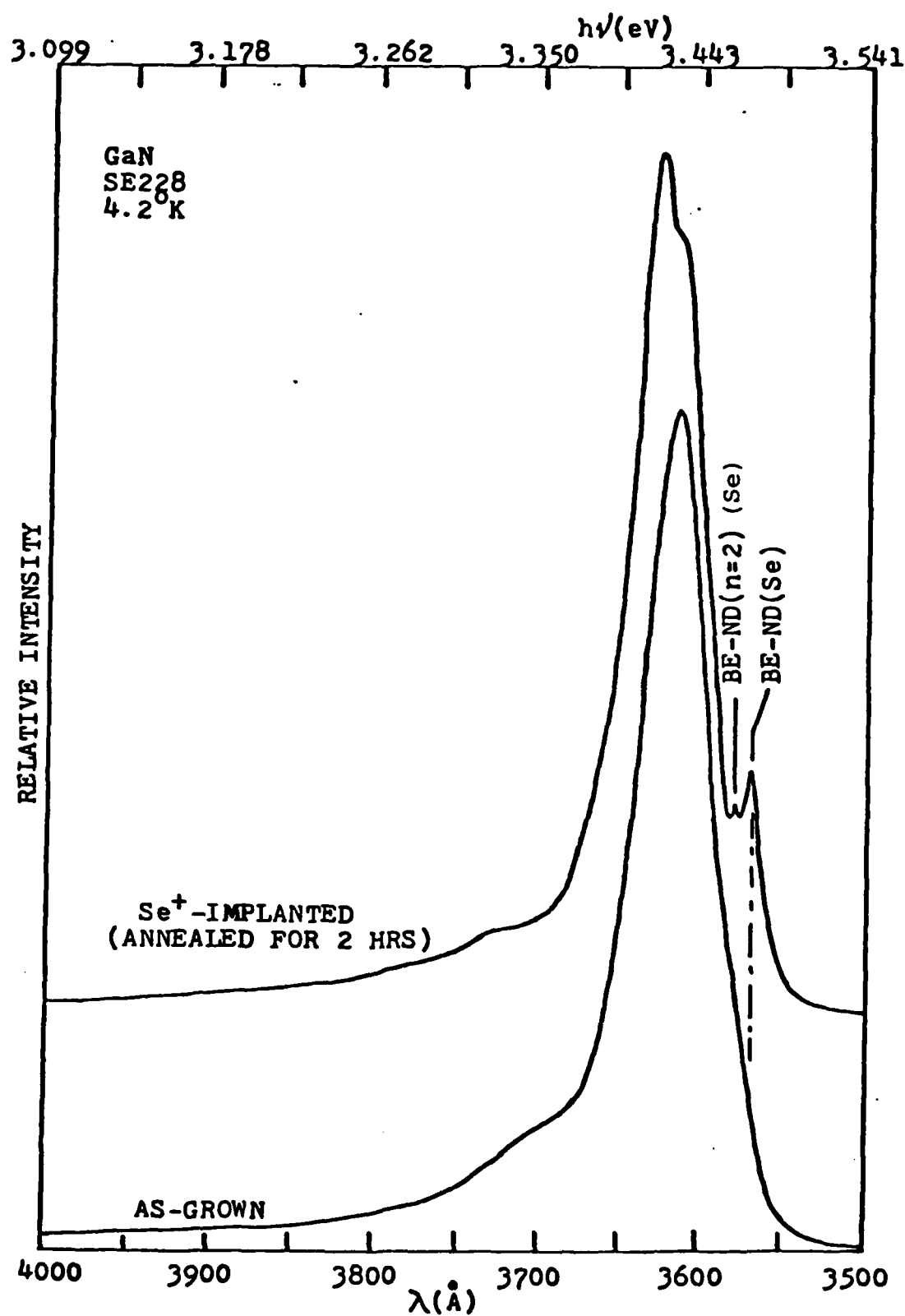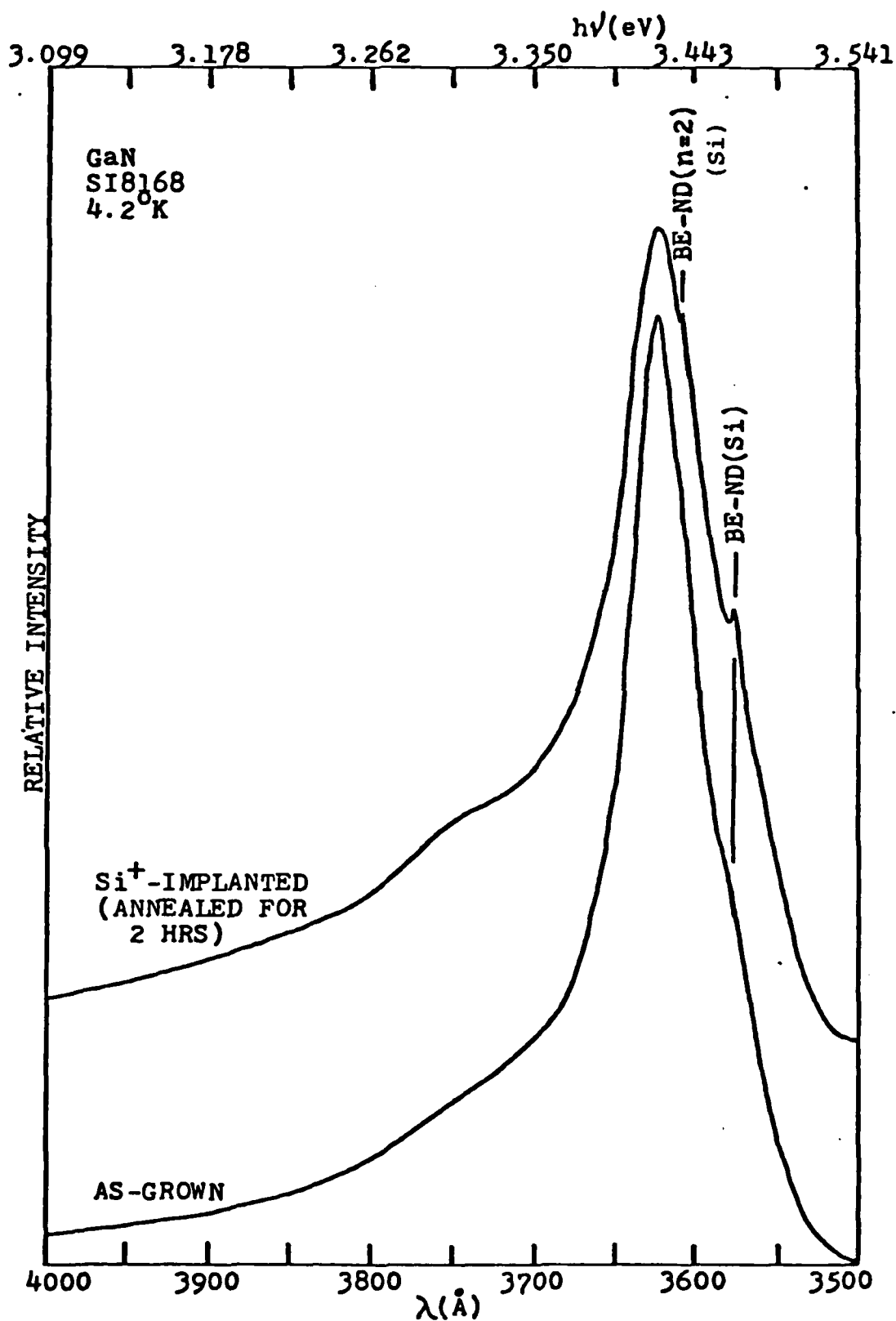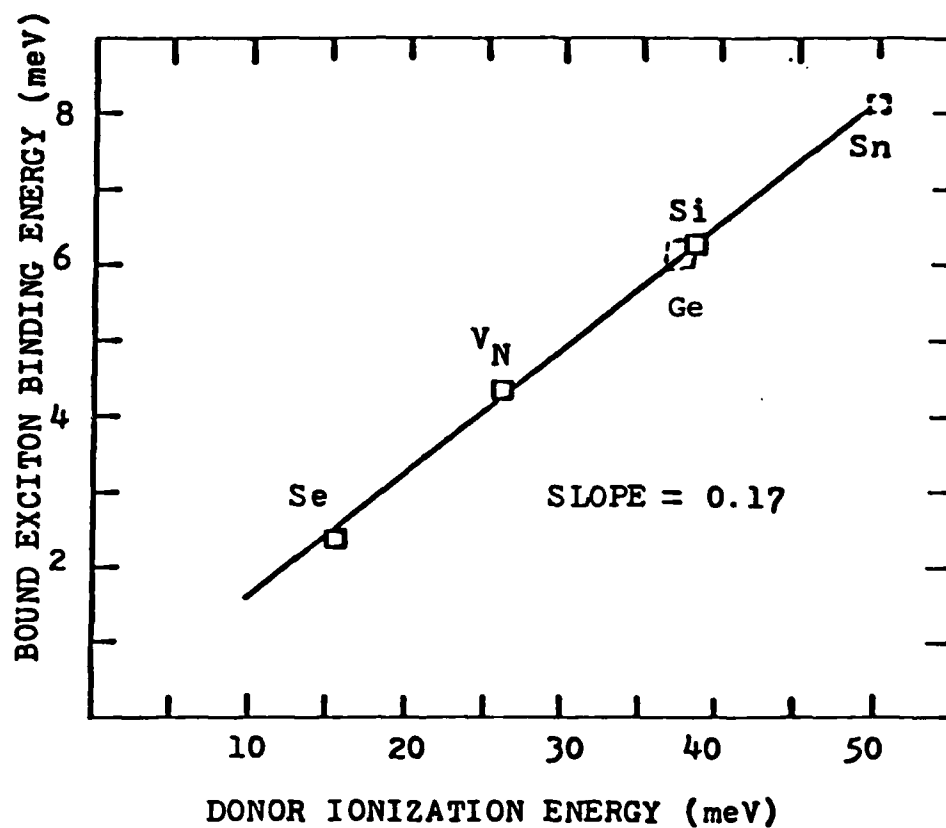Fig. 8
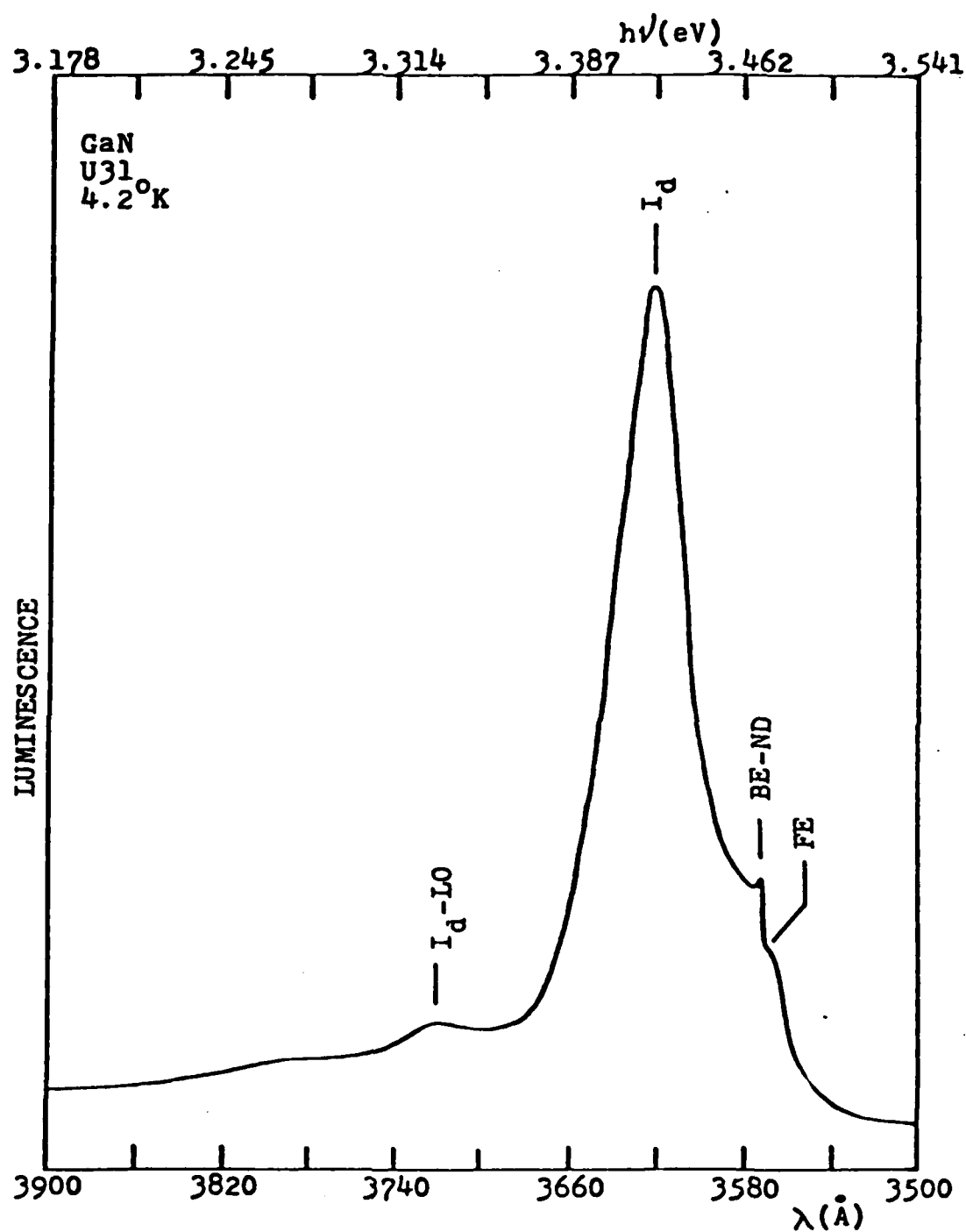
Luminescence of as-grown GaN

Fig. 9

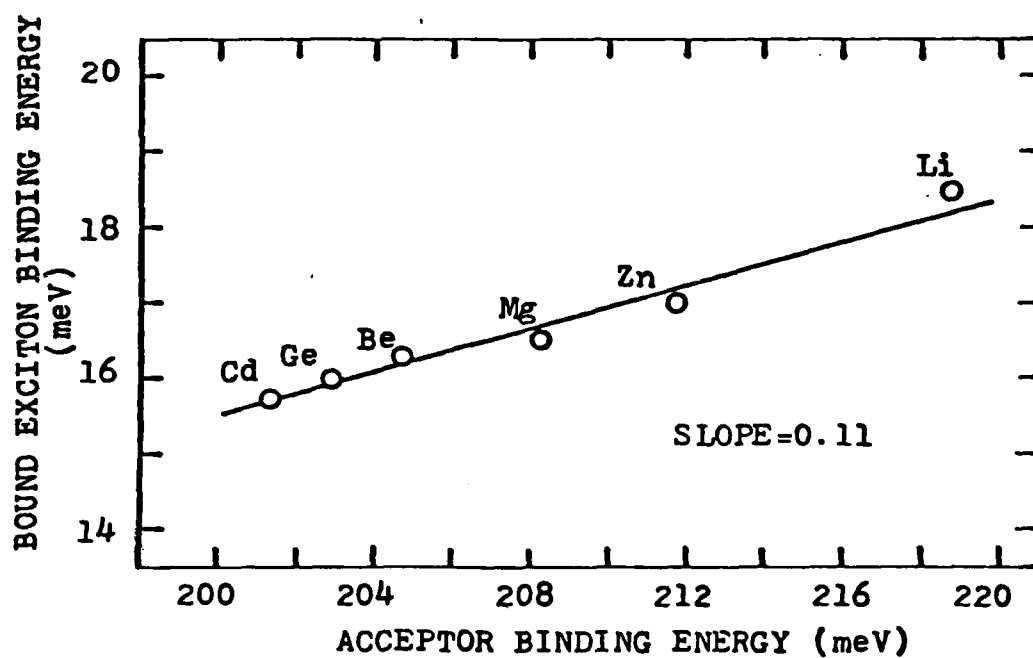Fig. 10

Luminescence of Se Implanted GaN

Luminescence of Si Implanted GaN

Fig. 11

Bound exciton to neutral donor binding
energy as a function of donor ionization
energy determined from two-electron
transition and effective mass approximation

Fig. 12

Bound exciton to neutral acceptor binding energy as a function of acceptor ionization energy determined from D-A emission

Fig. 13

END

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